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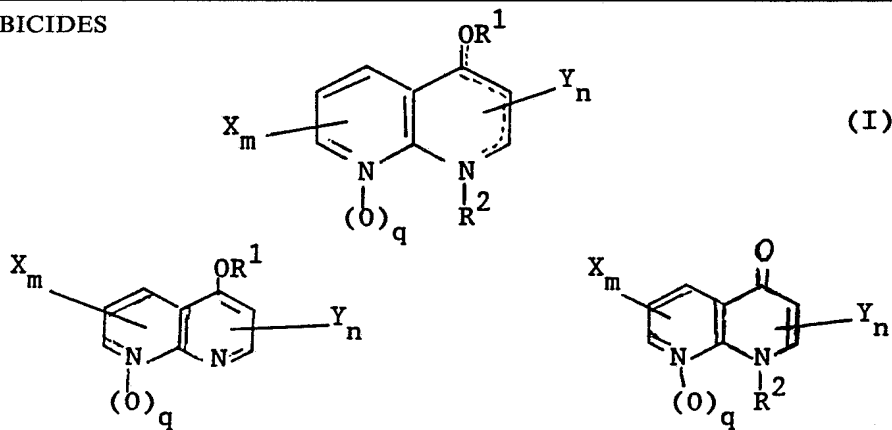
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(57) Abstract

A process of severely damaging or killing unwanted plants, which comprises applying to the plants, or to the growth medium of the plants, a herbicidally effective amount of a naphthyridine compound of formula (I), wherein either (a)  $R^1$  is a hydrogen atom, a lower acyl group, or an optionally substituted lower hydrocarbyl group, in which case no group  $R^2$  is present, or (b)  $R^2$  is a hydrogen atom, an optionally substituted lower hydrocarbyl group or a lower acyl group, in which case no group  $R^1$  is present; the dashed line between the oxygen atom and the nitrogen atom of the right-hand ring represents two double bonds which may be arranged either as in formula (Ia) or (Ib) and each of X and Y, which may be the same or different, may stand for fluorine, chlorine, bromine, or iodine; an optionally substituted lower hydrocarbyl group; an optionally substituted lower hydrocarbyl-thio, -sulphinyl, or -sulphonyl group; a carboxyl group or a salt, amide, or ester thereof; a cyano group; a nitro group; an  $-NR^3R^4$  group, wherein  $R^3$  and  $R^4$  may each stand independently for hydrogen, optionally substituted lower hydrocarbyl, lower alkylcarbonyl, lower alkoxy carbonyl or lower alkoxy, or  $R^3$  and  $R^4$ , together with the nitrogen atom to which they are attached, form a pyrrolidino, piperidino, or morpholino ring optionally substituted by one or more methyl groups; or each of X and Y may independently stand for an optionally substituted tri-, tetra- or penta-methylene group or a propenylene or butadienylene group wherein in the case of X the terminal valencies are attached to either the 5,6- or the 6,7-positions or in the case of Y to the 2,3-positions of the naphthyridine nucleus; m is 0, 1, 2 or 3; n is 0, 1 or 2; and q is 0 or 1.

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HERBICIDES

This invention relates to chemical compounds useful as herbicides, to processes for preparing them, and to herbicidal compositions and processes utilising them.

Published European Patent Application No. 329012 discloses certain arylsulphonamido (1,8) naphthyridines, proposed for use as herbicides.

For convenience in reference later in this specification, it is noted that the naphthyridine ring system is numbered as in formula (II), and that the 4H-pyrido [1,2-a] pyrimidin-4-one ring system is numbered as in formula (III). (All structural formulae are shown on a formula sheet at the end of this specification).

According to the present invention, there is provided a process of severely damaging or killing unwanted plants, which comprises applying to the plants, or to the growth medium of the plants, a herbicidally effective amount of a naphthyridine compound of the formula (I),

wherein either (a)  $R^1$  is a hydrogen atom, a lower acyl group, or an optionally substituted lower hydrocarbyl group, in which case no group  $R^2$  is present;

or (b)  $R^2$  is a hydrogen atom, an optionally substituted lower hydrocarbyl group or a lower acyl group, in which case no group  $R^1$  is present;

the dashed line between the oxygen atom and the nitrogen atom of the right-hand ring represents two double bonds which may be arranged either as in formula (Ia) or (Ib);

and each of X and Y, which may be the same or different, may stand for fluorine, chlorine, bromine, or iodine; an optionally substituted lower hydrocarbyl group; an optionally substituted lower hydrocarbyl-thio, -sulphinyl, or -sulphonyl group; a carboxyl group or a salt, amide, or ester thereof; a cyano group; a nitro group; an  $-NR^3R^4$  group wherein  $R^3$  and  $R^4$  may each stand independently for hydrogen, optionally substituted lower hydrocarbyl, lower alkylcarbonyl, lower alkoxy carbonyl or lower alkoxy, or  $R^3$  and  $R^4$ , together with the nitrogen atom to which they are attached, form a pyrrolidino, piperidino, or morpholino ring optionally substituted by one or more methyl groups; or each of X and Y may independently stand for an optionally substituted tri-, tetra-, or penta-methylene group or a propenylene or butadienylene group wherein in the case of X the terminal valencies are attached to either the 5,6- or the 6,7-positions or in the case of Y to the 2,3- positions of the naphthyridine nucleus;

m is 0, 1, 2, or 3;

n is 0, 1 or 2;

and q is 0 or 1;

It will be understood that when X or Y comprises a tri-, tetra-, or penta-methylene group or a propenylene or butadienylene group, the value of m or n is 2 and accordingly when X takes such a value only one other substituent X is possible in the left hand ring of formula I and when Y takes such a value, no other Y substituent is possible in the right hand ring.

The term lower hydrocarbyl used above, whether representing a substituent on its own or whether it is part of the definition of a larger group (e.g. as in hydrocarbyloxy, hydrocarbylthio etc) is intended to include hydrocarbyl groups having for example from 1 to 8 carbon atoms. A sub-class of such hydrocarbyl groups includes those having from 1 to 6 carbon atoms. A further subclass of such hydrocarbyl groups comprises those having from 1 to 4 carbon atoms. The term lower hydrocarbyl therefore includes for example C<sub>1-6</sub> alkyl including both straight and branched chain isomers (e.g. methyl, ethyl, propyl, and hexyl); cycloalkyl of 3 to 6 carbon atoms (e.g. cyclopropyl, cyclobutyl and cyclohexyl); C<sub>2</sub> to C<sub>6</sub> alkenyl including for example allyl and crotyl; C<sub>2</sub> to C<sub>6</sub> alkynyl (e.g. propynyl); phenyl; and benzyl.

When the lower hydrocarbyl moiety is substituted, there may be one or more substituents. Examples of substituents include halogen (i.e. fluorine, chlorine, bromine, and iodine); C<sub>1-4</sub> alkoxy; C<sub>1-4</sub> alkylthio; cyano; carboxy, and salts, amides and esters thereof; alkanoyl of 2 to 4 carbon atoms; and phenyl optionally substituted by one or more C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkoxy, C<sub>1-4</sub> alkylthio, nitro, fluorine, chlorine, bromine, cyano, or CF<sub>3</sub> groups.

When the lower hydrocarbyl radical is a substituted phenyl radical, the substituents may include one or more of the substituents listed in the last foregoing paragraph, and may also include nitro and optionally substituted alkyl.

The expression "salts, amides, and esters thereof" used above in relation to carboxy substitution includes for example salts formed from alkali metals (e.g. sodium, potassium, and lithium), alkaline earth metals (e.g. calcium and magnesium), the ammonium ion, and substituted ammonium ions wherein one, two, three, or four of the hydrogen atoms have been replaced by optionally substituted C<sub>1-6</sub> hydrocarbyl moieties as defined

above, and esters wherein the esterifying group comprises an optionally substituted hydrocarbyl radical of for example 1 to 20 carbon atoms. The esterifying group may be for example a  $C_{1-8}$  alkyl group, for example a methyl, ethyl, propyl or butyl group.

Where the esterifying group is substituted, there may be one or more substituents. Examples of substituents include those listed above in relation to the definition of the lower hydrocarbyl moiety.

Amide derivatives of the carboxyl group have the formula  $-CONR^3R^4$  wherein the groups  $R^3$  and  $R^4$  may have any of the values defined above.

The terms lower alkylcarbonyl and lower alkoxy carbonyl used above include for example alkylcarbonyl and alkoxy carbonyl radicals of from 2 to 6 carbon atoms. The term lower alkoxy includes alkoxy radicals of from 1 to 6, especially 1 to 4, carbon atoms.

The term lower acyl is intended to include for example alkylcarbonyl and alkoxy carbonyl radicals of 2 to 6 carbon atoms, and alkanesulphonyl radicals of 1 to 6 carbon atoms.

When  $R^1$  in formula I(a) or  $R^2$  in formula I(b) is a hydrogen atom, the naphthyridine compounds used in the process of the invention are capable of existing in two tautomeric forms, illustrated by formulae IVa and IVb below.

For convenience, compounds wherein  $R^1$  or  $R^2$  is H are denoted in this specification by only one of these formulae (usually formula IVb) but this formula is intended to cover both tautomers.

The compounds of formula (I) in which  $R^1$  is H form a subclass of compounds for use in the invention. Within this subclass, a further subclass comprises compounds in which X and Y comprise at least three methyl or ethyl groups.

A further sub-class of compounds for use in the invention comprises naphthyridine compounds of formula IVb wherein the group  $X_m$  comprises a  $C_{1-3}$  alkyl group in the 7-position of the naphthyridine ring, and a methyl or ethyl group in one or both of the 5- and 6- positions of the naphthyridine ring; and the group  $Y_n$  comprises a methyl or ethyl group at the 2- position and a  $C_{1-3}$  alkyl group or a bromine or iodine atom at the 3- position; or the group  $Y_n$  comprises a 1,4-tetramethylene or 1, 5-pentamethylene group linked to the 2- and the 3- position to form, together with the carbon atoms to which they are attached, a 6- or 7- membered ring.

Within the last mentioned sub-class, a further sub-class of compounds for use in the invention comprises compounds in which the 3- position is

occupied by a C<sub>1-3</sub> alkyl group.

Particular examples of compounds of formula (IVb, q=0) for use in the process of the invention are listed in Table I below:

TABLE 1

Compound No	X <sub>m</sub>	Y <sub>n</sub>
1	5,7-Me <sub>2</sub>	2-Me
2	5,7-Me <sub>2</sub>	2-Et
3	5,7-Me <sub>2</sub>	2-isoPr
4	5,7-Me <sub>2</sub>	2-Ph
5	5,7-Me <sub>2</sub>	2,3-Me <sub>2</sub>
6	5,7-Me <sub>2</sub>	2-Me,3-Et
7	5,7-Me <sub>2</sub>	2-Me,3-Pr
8	5,7-Me <sub>2</sub>	2-Me,3-Bu
9	5,7-Me <sub>2</sub>	2-Me,3-isoPr
10	5,7-Me <sub>2</sub>	2-Me,3-isoPrCH <sub>2</sub>
11	5,7-Me <sub>2</sub>	2-Me,3-isoPrCH <sub>2</sub> CH <sub>2</sub>
12	5,7-Me <sub>2</sub>	2-Me,3-Ph
13	5,7-Me <sub>2</sub>	2-Me,3-PhCH <sub>2</sub>
14	5,7-Me <sub>2</sub>	2,3-(CH <sub>2</sub> ) <sub>3</sub>
15	5,7-Me <sub>2</sub>	2,3-(CH <sub>2</sub> ) <sub>4</sub>
16	5,7-Me <sub>2</sub>	2-CF <sub>3</sub>
17	7-Me	2-Me
18	5,7-Me <sub>2</sub>	-
19	7-Me	-
20	-	2-Me
21	5,7-Me <sub>2</sub>	3-Cl
22	5,7-Me <sub>2</sub>	2-Me,3-Cl
23	7-Me	3-Cl
24	5,7-Me <sub>2</sub>	3-Br
25	7-Me	3-Br
26	5,7-Me <sub>2</sub>	2-Me,3-Br
27	5,7-Me <sub>2</sub>	2-CF <sub>3</sub> ,3-Br
28	5,7-Me <sub>2</sub>	3-I
29	see Note 1 at end of Table	

TABLE 1 continued

Compound No	X <sub>m</sub>	Y <sub>n</sub>
30	7-Me	2-Me, 3-Et
31	5,7-Me <sub>2</sub>	2,3-(CH <sub>2</sub> ) <sub>5</sub>
32	5,7-Me <sub>2</sub>	2-Et, 3-Me
33	5,7-Me <sub>2</sub>	2,3-Et <sub>2</sub>
34	5,6,7-Me <sub>3</sub>	2,3-Me <sub>2</sub>
35	5,6,7-Me <sub>3</sub>	2-Me, 3-Et
36	5,6,7-Me <sub>3</sub>	2-Me, 3-Pr
37	5,6,7-Me <sub>3</sub>	2-Me
38	6-Et, 5,7-Me <sub>2</sub>	2-Me, 3-Et
39	5,6,7-Me <sub>3</sub>	2,3-Et <sub>2</sub>
40	6,7-Me <sub>2</sub>	2-Me, 3-Et
41	5,6,7-Me <sub>3</sub>	2-Me, 3-Br
42	6-Br, 7-Me	2-Me, 3-Et
43	6-Br, 5,7-Me <sub>2</sub>	2,3-Me <sub>2</sub>
44	6-Br, 5,7-Me <sub>2</sub>	2-Me, 3-Et
45	6-Br, 5,7-Me <sub>2</sub>	3-Br
46a	5,7-Me <sub>2</sub>	2-CHCl <sub>2</sub> , 3-Me
46b	5,7-Me <sub>2</sub>	2-CH <sub>2</sub> Cl, 3-Me
47	see Note 2 at end of Table	
48	7-MeCOOCH <sub>2</sub> , 5-Me	2,3-Me <sub>2</sub>
49	7-CH <sub>2</sub> OH, 5-Me	2,3-Me <sub>2</sub>
50	5,6,7-Me <sub>3</sub>	2-Me, 3- <u>iso</u> Pr
51	6-Me, 7-Et	2-Me, 3-Et
52	6-Me, 7-Et	2-Me, 3- <u>iso</u> Pr
53	6-Me, 7-Et	2-CH <sub>2</sub> Br, 3-Et
54	5-Me, 7-CO <sub>2</sub> H	2,3-Me <sub>2</sub>
55	5-Me	2,3-Me <sub>2</sub>
56	See Note 3 at end of Table	
57	7-MeCOOCH <sub>2</sub> , 5-Me	2-Me, 3-Et
58	7-CH <sub>2</sub> OH, 5-Me	2-Me, 3-Et
59	5-Me, 7-CO <sub>2</sub> H	2-Me, 3-Et
60	5-Me	2-Me, 3-Et

TABLE 1 continued

Compound No	X <sub>m</sub>	Y <sub>n</sub>
61	6-Me-7-Et	2,3-Et <sub>2</sub>
62	5,7-Me <sub>2</sub> -6-Et	2-Me-3-Pr
63	5,7-Me <sub>2</sub> -6-Et	2,3-Et <sub>2</sub>
64	5,7-Me <sub>2</sub> -6-Et	2-Me-3-isoPr

Note 1 This compound is believed to have formula (XVI), but may have the alternative structure (XVIa)

Note 2 This compound has formula (XVII)

Note 3 This compound has formula (XVIII)



TABLE 2


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Proton magnetic resonance spectra of compounds of Table I.

Compound No.    Proton nuclear magnetic resonance spectrum

The solvent used was  $\text{CDCl}_3$ :  $d_6$  DMSO except where otherwise specified.

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1		$\delta$ 2.21(3H,s); 2.42(3H,s); 2.72(3H,s); 5.79(1H,s); 6.80(1H,s); 11.68(1H,broad s).
2		$\delta$ 1.18(3H,t); 2.40(3H,s); 2.51(2H,q); 2.71(3H,s); 5.80(1H,s); 6.80(1H,s); 11.62(1H,broad s).
3	( $\text{CDCl}_3$ )	$\delta$ 1.32(6H,d); 2.50(3H,s); 2.81(1H,m); 2.89(3H,s); 6.11(1H,s); 6.84(1H,s); 8.61(1H,broad s).
4		$\delta$ 2.53(3H,s); 2.85(3H,s); 6.30(1H,s); 6.90(1H,s); 7.50(3H,m); 7.80(2H,m); 11.83(1H,broad s).
5		$\delta$ 1.95(3H,s); 2.35(3H,s); 2.49(3H,s); 2.82(3H,s); 6.81(1H,s); 11.50(1H,broad s).
6		$\delta$ 1.03(3H, t); 2.36(3H,s); 2.48(3H,s); 2.49(2H,q); 2.82(3H,s); 6.80(1H,s); 11.48(1H,broad s).
7		$\delta$ 0.94(3H,t); 1.46(2H,m); 2.37(3H,s); 2.45(2H,m); 2.49(3H,s); 2.82(3H,s); 6.80(1H,s); 11.42(1H,broad s).
8		$\delta$ 0.92(3H,t); 1.39(4H,m); 2.35(3H,s); 2.42(2H,m); 2.46(3H,s); 2.81(3H,s); 6.81(1H,s); 11.52(1H,broad s).
9		$\delta$ 1.31(6H,d); 2.40(3H,s); 2.49(3H,s); 2.83(3H,s); 3.19(1H,m); 6.76(1H,s); 11.09(1H, broad s).
10	( $\text{CDCl}_3$ )	$\delta$ 0.92(6H,d); 1.97(1H,m); 2.36(3H,s); 2.41(2H,d); 2.50(3H,s); 2.90(3H,s); 6.82(1H,s); 8.52(1H,broad s).
11	( $\text{CDCl}_3$ )	$\delta$ 0.95(6H,d); 1.33(2H,m); 1.66(1H,m); 2.37(3H,s); 2.50(3H,s); 2.51(2H,m); 2.90(3H,s); 6.81(1H,s); 8.58(1H,broad s).

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TABLE 2 (continued)

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Proton magnetic resonance spectra of compounds of Table I.	
Compound No.	Proton nuclear magnetic resonance spectrum
	The solvent used was CDCl <sub>3</sub> : d <sub>6</sub> DMSO except where otherwise specified.
<hr/>	
12	δ 2.19(3H,s); 2.51(3H,s); 2.80(3H,s); 6.85(1H,s); 7.18-7.43(5H,m); 11.70(1H,broad s).
13 (CDCl <sub>3</sub> )	δ 2.32(3H,s); 2.51(3H,s); 2.91(3H,s); 3.95(2H,s); 6.84(1H,s); 7.09-7.30(5H,s).
14	δ 2.01(2H,m); 2.47(3H,s); 2.65(2H,t); 2.80(3H,s); 2.91(2H,t); 6.87(1H,s); 12.00(1H, broad s).
15	δ 2.71(4H,m); 2.33(2H,t); 2.46(3H,s); 2.61(2H,t); 2.79(3H,s); 6.84(1H,s); 11.52(1H,broad s).
17	δ 2.29(3H,s); 2.52(3H,s); 5.88(1H,s); 7.11(1H,d); 8.23(1H,d).
19	δ 2.61(3H,s); 6.17(1H,d); 7.18(1H,d); 7.72(1H,dd); 8.42(1H,d); 11.93(1H,broad s).
20	δ 2.41(3H,s); 6.03(1H,s); 7.30(1H,dd); 8.50(1H,dd); 8.66(1H,dd); 12.01(1H,broad s).
23	δ 2.68(3H,s); 6.75(1H,broad s); 7.27(1H,d); 8.10(1H,s); 8.58(1H,d).
24	δ 2.51(3H,s); 2.86(3H,s); 6.95(1H,s); 8.07(1H,s); 12.18(1H,broad s).
25	δ 2.61(3H,s); 7.23(1H,d); 8.15(1H,s); 8.48(1H,s); 12.41(1H,broad s).
30	δ 0.91(3H,t); 2.31(3H,s); 2.40(2H,q); 2.50(3H,s); 7.13 (1H,d); 8.23(1H,d); 11.78 (1H,broad s).
31	δ 1.35(2H,m); 1.55(2H,m); 1.72(2H,m); 2.40(3H,s); 2.61(2H,m); 2.71(3H,s); 2.74(2H,m); 6.86(1H,s); 11.63(1H,broad s).
32	δ 1.39(3H,t); 2.12(3H,s); 2.67(3H,s); 2.88(2H,q); 2.99(3H,s); 7.11(1H,s); 11.83(1H,broad s).
33	δ 1.01(3H,t); 1.22(3H,t); 2.45(2H,q); 2.47(3H,s); 2.67(2H,q); 2.80(3H,s); 6.92(1H,s); 11.61(H,broad s).

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TABLE 2 (continued)

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Proton magnetic resonance spectra of compounds of Table I.	
Compound No.	Proton nuclear magnetic resonance spectrum
	The solvent used was $\text{CDCl}_3$ : $\text{d}_6$ DMSO except where otherwise specified.
<hr/>	
34	$\delta$ 2.05(3H,s); 2.36(3H,s); 2.47(3H,s); 2.68(3H,s); 3.01(3H,s); 11.72(1H,broad s).
35	$\delta$ 0.96(3H,t); 2.19(3H,s); 2.31(3H,s); 2.42(2H,q); 2.50(3H,s); 2.85(3H,s); 11.49(1H,broad s).
36	$\delta$ 0.89(3H,t); 1.38(2H,m); 2.19(3H,s); 2.30(3H,s); 2.37(2H,m); 2.50(3H,s); 2.83(3H,s); 11.51(1H,broad s).
37	( $\text{CDCl}_3$ - $\text{d}_6$ DMSO - Trifluoroacetic acid); $\delta$ 2.49(3H,s); 2.74(3H,s); 2.79(3H,s); 2.99(3H,s); 6.98(1H,s).
38	$\delta$ 0.95(3H,t); 1.06(3H,t); 2.31(3H,s); 2.40(2H,q); 2.51(3H,t); 2.67(2H,q); 2.85(3H,s); 11.50 (1H,broad s).
39	$\delta$ 0.93(3H,t); 1.14(3H,t); 2.12(3H,s); 2.38(2H,q); 2.52(3H,s); 2.67(2H,q); 2.80(3H,s); 11.41(1H,broad s).
40	$\delta$ 1.02(3H,t); 2.35(3H,s); 2.38(3H,s); 2.52(2H,q); 2.54(3H,s); 8.16(1H,s); 11.71(1H,broad s).
41	( $\text{CDCl}_3$ - $\text{d}_6$ DMSO - trifluoroacetic acid): $\delta$ 2.22(3H,s); 2.48(3H,s); 2.51(3H,s); 2.82(3H,s).
42	$\delta$ 1.06(3H,t); 2.48(3H,s); 2.58(2H,q); 2.77(3H,s); 8.53 (1H,s); 12.17(1H,broad s).
43	$\delta$ 1.89(3H,s); 2.31(3H,s); 2.64(3H,s); 3.00(3H,s).
44	$\delta$ 0.98(3H,t); 2.31(3H,s); 2.44(2H,q); 2.65(3H,s); 3.00(3H,s).
45	( $\text{CDCl}_3$ - $\text{d}_6$ DMSO - trifluoroacetic acid) $\delta$ 2.61(3H,s); 2.99(3H,s); 8.30(1H,s); 12.52 (1H,broad s).
46a	( $\text{CDCl}_3$ ): $\delta$ 2.16(3H,s); 2.57(3H,s); 2.89(3H,s); 6.90(1H,s); 6.99(1H,s); 8.85(1H,broad s).
46b	( $\text{CDCl}_3$ - trifluoroacetic acid): $\delta$ 2.20(3H,s); 2.81(3H,s); 3.10(3H,s); 4.68(2H,s); 7.21(1H,s).
47	( $\text{CDCl}_3$ ): $\delta$ 2.08(3H,s); 2.48(3H,s); 2.65(3H,s); 2.89(3H,s); 6.90(1H,s); 10.48(1H,broad s).

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TABLE 2 (continued)

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Proton magnetic resonance spectra of compounds of Table I.	
Compound No.	Proton nuclear magnetic resonance spectrum
	The solvent used was $\text{CDCl}_3$ : $\text{d}_6$ DMSO except where otherwise specified.
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48	( $\text{CDCl}_3$ ): $\delta$ 2.03(3H,s); 2.20(3H,s); 2.39(3H,s); 2.96(3H,s); 5.15(2H,s); 6.99(1H,s); 8.69(1H,broad s).
49	$\delta$ 2.04(3H,s); 2.41(3H,s); 2.95(3H,s); 4.36(1H,t); 4.72(2H,d); 6.97(1H,s); 10.51(1H,broad s).
50	( $\text{CDCl}_3$ ): $\delta$ 1.35(6H,d); 2.26(3H,s); 2.35(3H,s); 2.93(3H,s); 3.21(1H,m); 8.78(1H,broad s).
51	$\delta$ 0.91(3H,t); 1.20(3H,t); 2.28(3H,s); 2.29(3H,s); 2.41(2H,q); 2.78(2H,q); 8.05(1H,s); 11.68 (1H,broad s).
52	$\delta$ 1.18(3H,t); 1.21(6H,d); 2.30(3H,s); 2.33(3H,s); 2.78(2H,q); 3.01(1H,m); 8.01(1H,s); 11.55(1H,broad s).
53	$\delta$ 1.01(3H,t); 1.22(3H,t); 2.31(3H,s); 2.50(2H,q); 2.80(2H,t); 4.61(2H,s); 8.07(1H,s); 11.98(1H,broad s).
54	$\delta$ 1.90(3H,s); 2.32(3H,s); 2.88(3H,s); 7.62(1H,s); 12.12(1H,broad s).
55	( $\text{CDCl}_3$ ): $\delta$ 2.06(3H,s); 2.44(3H,s); 2.96(3H,s); 7.01(1H,d); 8.42(1H,broad d); 11.59(1H,broad).
56	( $\text{CDCl}_3$ ): $\delta$ 1.10(3H,t); 2.47(3H,s); 2.59(2H,q); 2.88(3H,s); 6.88(1H,s); 10.22 (1H,broad s).
57	( $\text{CDCl}_3$ ) inter alia: $\delta$ 1.08(3H,t); 2.20(3H,s); 2.39(3H,s); 2.96(3H,s); 5.15(2H,s); 6.98(1H,s); 8.52 (1H,broad s).
58	( $\text{CDCl}_3$ ): $\delta$ 1.09(3H,t); 2.42(3H,s); 2.58(2H,q); 2.95 (3H,s); 3.68(1H,t); 4.74 (2H,d); 6.88(1H,s); 8.63(1H,broad s).
60	( $\text{CDCl}_3$ ): $\delta$ 1.12(3H,t); 2.43(3H,s); 2.60(2H,q); 2.98(3H,s); 6.99(1H,d); 8.38(1H,d); 9.71(1H,broad s).
61	$\delta$ 1.00(3H,t); 1.21(3H,t); 1.25(3H,t); 2.35(3H,s); 3.47(2H,q); 2.67(2H,q); 2.82(2H,q); 5.31(1H,broad); 8.10(1H,s).
62	$\delta$ 0.87(3H,t); 1.07(3H,t); 1.38(2H,m); 2.29(3H,s); 2.35(2H,m); 2.51(3H,s); 2.68(2H,m); 2.85(3H,s); 11.50(1H,broad).

---

TABLE 2 (continued)

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Proton magnetic resonance spectra of compounds of Table I.	
Compound No.	Proton nuclear magnetic resonance spectrum
	The solvent used was $\text{CDCl}_3$ : $\text{d}_6$ DMSO except where otherwise specified.
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63	$\delta$ 0.98(3H,t); 1.05(3H,t); 1.16(3H,t); 2.40(2H,q); 2.50(3H,s); 2.55-2.72(4H,m); 2.84(3H,s); 11.44(1H,broad).
64	( $\text{CDCl}_3$ ): $\delta$ 1.11(3H,t); 1.35(6H,d); 2.36(3H,s); 2.55(3H,s); 2.72(2H,q); 2.92(3H,s); 3.20(2H,m); 8.19(1H,broad).

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Certain of the compounds listed above are new, and these form a further part of the invention.

In another aspect, therefore, the invention provides naphthyridine compounds of the formula (IVb) wherein the group  $X_m$  comprises a  $C_{1-3}$  alkyl substituent in the 7-position of the naphthyridine ring, and a methyl or ethyl group in one or both of the 5- and 6- positions; and the group  $Y_n$  comprises a methyl or ethyl substituent at the 2- position of the naphthyridine ring; a  $C_{1-3}$  alkyl substituent or a bromo or iodo substituent at the 3- position; or the group  $Y_n$  comprises a 1,4-tetramethylene or 1,5-pentamethylene group linked to the 2- and the 3- position to form, together with the carbon atoms to which they are attached, a 6- or 7- membered ring, provided that the compounds 2,3,5,7- tetramethyl-1,8- naphthyridin-4-one and 3-ethyl-2,5,7- trimethyl-1,8- naphthyridin-4-one are excluded.

Within the class of compounds defined above, a sub-class comprises those compounds in which the 3- position of the naphthyridine ring bears a  $C_{1-3}$  alkyl substituent.

Compounds for use in the process of the invention which have a substituent in the 7-position may be prepared by thermal rearrangement of a correspondingly 6-substituted 4H-pyrido[1,2-a]pyrimidin-4-one. An example is shown in Scheme A below.

The 6-substituted 4H-pyrido[1,2-a]pyrimidin-4-ones required for Scheme A may be prepared by condensation of an appropriately substituted beta-keto ester or enol ether thereof with a 2-amino-6-substituted pyridine, according to known procedures. By way of example, the pyrimidinone (V) may be prepared by condensation of ethyl acetoacetate with

2-amino-6-methylpyridine according to known procedures. The 7-substituted naphthyridinones prepared by the process of Scheme A may be submitted to further chemical processes to introduce additional substituents or to remove or modify substituents already present, according to known chemical procedures.

Thus, for example, a 3-chloro or 3-bromo substituent may be introduced by treating a 3-unsubstituted naphthyridin-4-one with a chlorinating or brominating agent, and a 3,6-dibromonaphthyridin-4-one may be prepared for example by treating a 3,6-unsubstituted naphthyridin-4-one with bromine. Bromination of a 3-substituted naphthyridin-4-one can be used to obtain a 6-bromo naphthyridin-4-one. 2-Mono and dichloromethyl naphthyridinones may be prepared by sulphuryl chloride treatment of 2-methyl naphthyridinones.

The N-oxides of formula I may be obtained in the conventional way by treating the corresponding nitrogen compounds with per-acids, for example meta-chloroperbenzoic acid as illustrated in Example 21. The N-oxides of the 7-methyl substituted naphthyridinones of formula (I) can be converted to the corresponding 7-acetoxymethyl derivatives by treatment with acetic anhydride, as illustrated in Example 22. The 7-acetoxymethyl derivatives so obtained may be hydrolysed to the corresponding 7-hydroxymethyl compounds and these in turn may be oxidised to the 7-carboxy naphthyridinones and decarboxylated to give the 7-unsubstituted compounds, as illustrated in Examples 23, 25 and 26.

Compounds of formula I having no substituent in the 7-position cannot in general be made directly by the process exemplified in Scheme A above, since the intermediate 4H-pyrido[1,2-a]pyrimidin-4-one will not undergo the required thermal rearrangement unless a substituent is present in the 6-position of the latter.

However, highly substituted compounds, for example compound 34 of Table I, which has substituents in the 5, 6 and 7 positions, may be prepared without isolation of the intermediate 4H-pyrido[1,2-a] pyrimidin-4-one since the thermal rearrangement of the highly substituted intermediate proceeds readily in the polyphosphoric acid used as the reaction medium for the initial condensation of the substituted 2-aminopyridine and the substituted beta keto ester.

According to a further feature of the invention, there is provided a process which enables the preparation of compounds of formula I having no substituent in the 7-position, as well as 7-substituted compounds. The process is outlined in Scheme B below.

According to step (a) of Scheme B, a pyrido-oxazine (VII), where  $X_m$  is as defined above for formula (I), is reacted with a beta keto ester derivative (VIII) in the presence of a base, at an elevated temperature, to give the naphthyridinone derivative (IX). The group  $R^5$  of the beta keto ester derivative (VIII) stands for an optionally substituted lower hydrocarbonyl group as defined above for the group Y. It may be, for example, an alkyl group of 1 to 4 carbon atoms. The group  $R^6$  stands for an esterifying group as defined above in relation to esters of carboxy group substituents, and may be for example methyl or ethyl.

By elevated temperature is meant a temperature of about 80-150°C, preferably from 110-130°C. Following the completion of the reaction, the reaction mixture is cooled and neutralised and the naphthyridinone derivative (X) isolated by conventional procedures.

In step (b) of Scheme B, the naphthyridinone derivative (IX) is hydrolysed to the corresponding carboxylic acid, for example by heating it in aqueous alcohol solution with an alkali metal hydroxide. On completion of the reaction, the mixture is cooled and acidified and the carboxylic acid (X) recovered by conventional procedures.

According to step (c) of Scheme B, the carboxylic acid (X) may be decarboxylated by heating to its melting point until evolution of gas ceases. The naphthyridinone derivative (XI) so obtained may be purified by conventional methods (e.g. recrystallisation). If desired, the naphthyridinone derivative (XI) may be subjected to further chemical reactions in order to introduce additional substituents or to remove or modify substituents already present.

The starting material (VII) for Scheme B may itself be prepared by lead tetra-acetate treatment of a 2-carbamoylnicotinic acid derivative (XII) as shown in Scheme C below:

In Scheme C,  $X_m$  is as defined as above for formula (I). The reaction is carried out at an elevated temperature (e.g. about 50-100°C, preferably at 60-70°C) in a solvent or diluent for the reactants.

The 2-carbamoylnicotinic acid derivative (XII) required as starting material for Scheme C, may itself be prepared by treating the appropriate quinolinic anhydride derivative (XIII) with ammonia.

The group  $X_m$  in formula (XIII) is defined as for formula (I).

The starting materials for the above schemes A, B and C are either known, or if not known, may be prepared by known synthetic procedures using the appropriate starting materials. Thus, the substituted 2-amino

pyridines required for scheme A may be prepared for example by reacting a suitably substituted pentane-1,3-dione with malonamamide, to give a carbamoyl substituted pyridine of formula (XIV).

The carbamoyl - substituted pyridine (XIV) may then be hydrolysed to the corresponding carboxylic acid, and this then decarboxylated to give the required substituted 2-amino pyridine (XV).

The following preparative Examples A to G illustrate the preparation of certain intermediates required for the preparation of the compounds in the Examples.

#### Preparative Example A

##### Preparation of ethyl 2-methylpropionylacetate

Ethyl propionylacetate (15.00g) was added dropwise to a solution of sodium metal (3.00g) in methanol (50ml). The resulting solution was stirred for 20 minutes then methyl iodide (18.68g) was added dropwise. The mixture was then heated under reflux for 4 hours, then cooled, and acidified to pH1 using 2M hydrochloric acid, sodium bisulphite (ca 2g) was added to remove any iodine, then the mixture was extracted with diethyl ether (x3). The combined ether extracts were washed with brine, dried ( $\text{MgSO}_4$ ), and evaporated in vacuo to leave a clear liquid. This was distilled under reduced pressure to afford ethyl 2-methylpropionyl acetate as a clear liquid, contaminated with some methyl 2-methyl propionyl acetate. This mixture was used without further purification.

#### Preparative Example B

##### Preparation of Ethyl 2-ethylpropionylacetate.

By a procedure similar to that described in the foregoing paragraph, but using ethyl propionylacetate (15.00g), sodium metal (3.03g), ethanol (50ml) and ethyl iodide (20.58g), ethyl 2-ethylpropionylacetate was obtained as a clear liquid, yield 10.81g.

#### Preparative Example C

##### Preparation of 2-Amino-4,5,6-trimethylpyridine

##### Step A: 2-Amino-4,5,6-trimethylpyridine-3-carboxamide

A solution of sodium hydroxide (24.30g) in water (243ml) was added dropwise to a stirred mixture of malonamamide hydrochloride (83.00g) and 3-methylpentane-2,4-dione (68.83g). The mixture was stirred for sixteen hours, then the white precipitate was filtered off and dried, to give the title compound as a white powder.

H nmr data ( $\text{CDCl}_3$ - $d_6$ DMSO):  $\delta$  2.01 (3H,s); 2.09 (3H,s); 2.21 (3H,s); 5.25 (2H, broad s); 7.51 (1H, broad s); 7.71 (1H, broad s).



Step B: 2-Amino-4,5,6-trimethylpyridine

A solution of 2-amino-4,5,6-trimethylpyridine-3-carboxamide (prepared in step A above) in 80% sulphuric acid (140ml) was heated to 140°C for five hours. The mixture was then cooled, poured onto cracked ice, and made alkaline using 6M sodium hydroxide solution. This was extracted with ethyl acetate, which was separated, washed with brine, water, and then dried ( $\text{MgSO}_4$ ). Evaporation in vacuo gave 2-amino-4,5,6-trimethyl pyridine as a pale brown solid, yield 24.00g.

$^1\text{H}$  nmr data ( $\text{CDCl}_3$ ):  $\delta$  2.08 (3H,s); 2.16(3H,s); 2.36 (3H,s); 4.12 (2H, broad s); 6.20 (1H,s).

Preparative Example DPreparation of 2-Amino-5-ethyl-4,6-dimethylpyridineStep A: 2-Amino-5-ethyl-4,6-dimethylpyridine-3-carboxamide

By a procedure similar to that described in preparative Example C, step A but using 3-ethylpentane-2,4-dione (50.00g), malonamamide hydrochloride (53.31g), sodium hydroxide (17.18g) and water (172ml), the title compound was obtained as a white solid.

$^1\text{H}$  nmr data ( $\text{CDCl}_3$ - $\text{d}_6$ DMSO):  $\delta$  0.95 (3H,t); 2.09 (3H,s); 2.21 (3H,s); 2.41 (2H,q); 5.21 (2H, broad s); 7.43 (1H broad s); 7.75 (1H, broad s).

Step B: 2-Amino-5-ethyl-4,6-dimethylpyridine

By a procedure similar to that described in Preparative Example C, step B but using 2-amino-5-ethyl-4,6-dimethylpyridine-3-carboxamide (prepared in step A, above) and 80% sulphuric acid (70ml), the title compound was obtained, yield 2.80g.

$^1\text{H}$  nmr data ( $\text{CDCl}_3$ ):  $\delta$  1.07 (3H,t); 2.19 (3H); 2.37(3H,s); 2.52 (2H,q); 4.20 (2H, broad s); 6.20 (1H,s).

Preparative Example EPreparation of 2-Amino-5,6-dimethylpyridineStep A: 2-Amino-5,6-dimethylpyridine-3-carboxamide

By a procedure similar to that described in Preparative Example C, step A but using 3-formyl-2-butanone (Tracy and Elderfield, J. Org. Chem 1941, 6, 62)(6.00g) malonamamide hydrochloride (8.22g), sodium hydroxide (2.63g) and water (26ml), the title compound was obtained as a pale yellow solid.

$^1\text{H}$  nmr data ( $\text{CDCl}_3$  -  $d_6$  DMSO):  $\delta$  2.02(3H,s); 2.30(3H,s); 6.81(2H,broad s); 7.09(1H,broad s); 7.66(1H,s); 7.75(1H,broad s).

Step B: 2-Amino-5,6-dimethylpyridine

By a procedure similar to that described in Preparative Example C, step B, but using 2-amino-5,6-dimethylpyridine-3-carboxamide (prepared in Step A, above) and 80% hydrochloric acid (10ml), pyrolysis of the resultant product using a gas burner, extraction of the residue with ethyl acetate, and evaporation of the extract in vacuo, the title compound was obtained as a brown solid, yield 1.23g.

$^1\text{H}$  NMR data ( $\text{CDCl}_3$ ):  $\delta$  2.15(3H,s); 2.33(3H,s); 4.35(2H,broad); 6.29(1H,d); 7.18(1H,d).

Preparative Example F

Preparation of 2-Amino-6-ethyl-5-methyl-pyridine

Step A: 2-Amino-6-ethyl-5-methyl-pyridine-3-carboxamide

By a procedure similar to that described in Preparative Example C, step A but using 2-formylpentan-3-one (prepared as in Preparative Example G, below) (57.86g), malonamidine hydrochloride (51.26g), sodium hydroxide (24.36g) and water (50ml), the title compound was obtained as a pale yellow solid, yield 49.14g.

$^1\text{H}$  NMR data ( $\text{CDCl}_3$ ):  $\delta$  1.21(3H,t); 2.19(3H,s); 2.68(2H,q); 5.69 (2H,broad); 6.28(2H,broad); 7.37(1H,s).

Step B: 2-Amino-6-ethyl-5-methylpyridine

By a procedure similar to that used in Preparative Example C, step B, but using 2-amino-6-ethyl-5-methylpyridine-3-carboxamide (prepared in step A, above) (48.05g) and 80% sulphuric acid (100ml), the title compound was obtained as a yellow gum, yield 22.16g.

$^1\text{H}$  NMR data ( $\text{CDCl}_3$ ):  $\delta$  1.21(3H,t); 2.17(3H,s); 2.64(2H,q); 4.44(2H,broad); 6.28(1H,d); 7.15(1H,d).

Preparative Example G

Preparation of 2-Formylpentan-3-one.

A solution of pentan-3-one (86.00g) and ethyl formate (74.00g) in diethyl ether (400ml) was cooled to 0°C (bath temperature) and stirred vigorously while sodium metal (23.00g) was added portion wise over 1 hour. The mixture was then allowed to warm to room temperature, and was stirred for

16 hours. The precipitate was filtered off, washed with diethyl ether, then added to 2M hydrochloric acid. This was then extracted with diethyl ether (X3). The combined ether extracts were dried ( $\text{MgSO}_4$ ) and the ether was then removed by distillation at atmospheric pressure using a Vigreux column. The residue in the distillation pot was the crude title compound, obtained as a red oil, yield 57.86g. This was used without further purification.

2-Formylpentan-3-one can exist in various tautomeric forms.

$^1\text{H}$  NMR data ( $\text{CDCl}_3$ ); (major enol form only):  $\delta$  1.19(3H,t); 1.88(3H,s); 2.55(2H,q); 7.67(1H,broad s); 14.68(1H,broad).

The compounds of formula (I) are active against a broad range of weed species including monocotyledonous and dicotyledonous species. They show some selectivity towards certain species; they may be used, for example, as selective herbicides in soya-bean crops. The compounds of formula (I) are preferably applied directly to unwanted plants (post-emergence application) but they may also be applied to the soil before the unwanted plants emerge (pre-emergence application).

The compounds of formula (I) may be used on their own to kill or severely damage plants, but are preferably used in the form of a composition comprising a compound of formula (I) in admixture with a carrier comprising a solid or liquid diluent.

Compositions containing compounds of formula (I) include both dilute compositions, which are ready for immediate use, and concentrated compositions, which require to be diluted before use, usually with water. Preferably the compositions contain from 0.01% to 90% by weight of the active ingredient. Dilute compositions ready for use preferably contain from 0.01 to 2% of active ingredient, while concentrated compositions may contain from 20 to 90% of active ingredient, although from 20 to 70% is usually preferred.

The solid compositions may be in the form of granules, or dusting powders wherein the active ingredient is mixed with a finely divided solid diluent, e.g. kaolin, bentonite, kieselguhr, dolomite, calcium carbonate, talc, powdered magnesia, Fuller's earth and gypsum. They may also be in the form of dispersible powders or grains, comprising a wetting agent to facilitate the dispersion of the powder or grains in liquid. Solid compositions in the form of a powder may be applied as foliar dusts.

Liquid compositions may comprise a solution or dispersion of an active ingredient in water optionally containing a surface-active agent, or may

comprise a solution or dispersion of an active ingredient in a water-immiscible organic solvent which is dispersed as droplets in water.

Surface-active agents may be of the cationic, anionic, or non-ionic type or mixtures thereof. The cationic agents are, for example, quaternary ammonium compounds (e.g. cetyltrimethylammonium bromide). Suitable anionic agents are soaps; salts of aliphatic mono ester of sulphuric acid, for example sodium lauryl sulphate; and salts of sulphonated aromatic compounds, for example sodium dodecylbenzenesulphonate, sodium, calcium, and ammonium lignosulphonate, butylnaphthalene sulphonate, and a mixture of the sodium salts of diisopropyl and triisopropyl naphthalenesulphonic acid. Suitable non-ionic agents are the condensation products of ethylene oxide with fatty alcohols such as oleyl alcohol and cetyl alcohol, or with alkylphenols such as octyl- or nonyl- phenol (e.g. Agral 90) or octyl-cresol. Other non-ionic agents are the partial esters derived from long chain fatty acids and hexitol anhydrides, for example sorbitan monolaurate; the condensation products of the partial ester with ethylene oxide; the lecithins; and silicone surface active agents (water soluble surface active agents having a skeleton which comprises a siloxane chain e.g. Silwet L77). A suitable mixture in mineral oil is Atplus 411F.

The aqueous solutions or dispersions may be prepared by dissolving the active ingredient in water or an organic solvent optionally containing wetting or dispersing agent(s) and then, when organic solvents are used, adding the mixture so obtained to water optionally containing wetting or dispersing agent(s). Suitable organic solvents include, for example, ethylene di-chloride, isopropyl alcohol, propylene glycol, diacetone alcohol, toluene, kerosene, methylnaphthalene, the xylenes and trichloroethylene.

The compositions for use in the form of aqueous solutions or dispersions are generally supplied in the form of a concentrate containing a high proportion of the active ingredient, and the concentrate is then diluted with water before use. The concentrates are usually required to withstand storage for prolonged periods and after such storage, to be capable of dilution with water to form aqueous preparations which remain homogeneous for a sufficient time to enable them to be applied by conventional spray equipment. Concentrates conveniently contain 20-90%, preferably 20-70%, by weight of the active ingredient(s). Dilute preparations ready for use may contain varying amounts of the active ingredient(s) depending upon the intended purpose; amounts of 0.01% to

10.0% and preferably 0.1% to 2%, by weight of active ingredient(s) are normally used.

A preferred form of concentrated composition comprises the active ingredient which has been finely divided and which has been dispersed in water in the presence of a surface-active agent and a suspending agent. Suitable suspending agents are hydrophilic colloids and include, for example, polyvinylpyrrolidone and sodium carboxymethylcellulose, and the vegetable gums, for example gum acacia and gum tragacanth. Preferred suspending agents are those which impart thixotropic properties to, and increase the viscosity of the concentrate. Examples of preferred suspending agents include hydrated colloidal mineral silicates, such as montmorillonite, beidellite, nontronite, hectorite, saponite, and saucorite. Bentonite is especially preferred. Other suspending agents include cellulose derivatives and polyvinyl alcohol.

The rate of application of the compounds of the invention will depend on a number of factors including, for example, the compound chosen for use, the identity of the plants whose growth is to be inhibited, the formulations selected for use and whether the compound is to be applied for foliage or root uptake. As a general guide, however, an application rate of from 0.001 to 20 kilograms per hectare is suitable while from 0.025 to 10 kilograms per hectare may be preferred.

The compositions of the invention may comprise, in addition to one or more compounds of the invention, one or more compounds not of the invention but which possess biological activity. Accordingly in yet a still further embodiment the invention provides a herbicidal composition comprising a mixture of at least one herbicidal compound of formula (I) as hereinbefore defined with at least one other herbicide.

The other herbicide may be any herbicide not having the formula (I). It will generally be a herbicide having a complementary action in the particular application.

Examples of useful complementary herbicides include:

- A. benzo-2,1,3-thiadiazin-4-one-2,2-dioxides such as bentazone;
- B. hormone herbicides, particularly the phenoxy alkanoic acids such as MCPA, MCPA-thioethyl, dichlorprop, 2,4,5-T, MCPB, 2,4-D, 2,4-DB, mecoprop, trichlopyr, clopyralid, and their derivatives (eg. salts, esters and amides);
- C. 1,3 dimethylpyrazole derivatives such as pyrazoxyfen, pyrazolate and benzofenap;

- D. Dinitrophenols and their derivatives (eg. acetates) such as dinoterb, dinoseb and its ester, dinoseb acetate;
- E. dinitroaniline herbicides such as dinitramine, trifluralin, ethalflurolin, pendimethalin, oryzalin;
- F. arylurea herbicides such as diuron, flumeturon, metoxuron, neburon, isoproturon, chlorotoluron, chloroxuron, linuron, monolinuron, chlorobromuron, daimuron, methabenzthiazuron;
- G. phenylcarbamoxyloxyphenylcarbamates such as phenmedipham and desmedipham;
- H. 2-phenylpyridazin-3-ones such as chloridazon and norflurazon;
- I. uracil herbicides such as lenacil, bromacil and terbacil;
- J. triazine herbicides such as atrazine, simazine, aziprotryne, cyanazine, prometryn, dimethametryn, simetryne, and terbutryn;
- K. phosphorothioate herbicides such as piperophos, bensulide, and butamifos;
- L. thiolcarbamate herbicides such as cycloate, vernolate, molinate, thiobencarb, butylate\*, EPTC\*, tri-allate, di-allate, esprocarb, tiocarbazil, pyridate, and dimepiperate;
- M. 1,2,4-triazin-5-one herbicides such as metamitron and metribuzin;
- N. benzoic acid herbicides such as 2,3,6-TBA, dicamba and chloramben;
- O. anilide herbicides such as pretilachlor, butachlor, alachlor, propachlor, propanil, metazachlor, metolachlor, acetochlor, and dimethachlor;
- P. dihalobenzonitrile herbicides such as dichlobenil, bromoxynil and ioxynil;
- Q. haloalkanoic herbicides such as dalapon, TCA and salts thereof;
- R. diphenylether herbicides such as lactofen, fluroglycofen or salts or ester thereof, nitrofen, bifenox, acifluorfen and salts and esters thereof, oxyfluorfen, fomesafen, chlornitrofen and chlomethoxyfen;
- S. phenoxyphenoxypropionate herbicides such as diclofop and esters thereof such as the methyl ester, fluazifop and esters thereof, haloxyfop and esters thereof, quizalofop and esters thereof and fenoxaprop and esters thereof such as the ethyl ester;
- T. cyclohexanedione herbicides such as alloxymid and salts thereof, sethoxydim, cycloxydim, tralkoxydim, and clethodim;

- U. sulfonyl urea herbicides such as chlorosulfuron, sulfometuron, metsulfuron and esters thereof; benzsulfuron and esters thereof such as DPX-M6313, chlorimuron and esters such as the ethyl ester thereof, pirimisulfuron and esters such as the methyl ester thereof, 2-[3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-3-methylureidosulphonyl] benzoic acid esters, such as the methyl ester thereof (DPX-LS300), and pyrazosulfuron;
- V. imidazolidinone herbicides such as imazaquin, imazamethabenz, imazapyr and isopropylammonium salts thereof, imazethapyr;
- W. arylanilide herbicides such as flamprop and esters thereof, benzoylprop-ethyl, diflufenican;
- X. amino acid herbicides such as glyphosate and glufosinate and their salts and esters, sulposate and bialaphos;
- Y. organoarsenical herbicides such as monosodium methanearsonate (MSMA);
- Z. herbicidal amide derivative such as napropamide, propyzamide, carbetamide, tebutam, bromobutide, isoxaben, naproanilide and naptalam;
- AA. miscellaneous herbicides including ethofumesate, cinmethylin, difenzoquat and salts thereof such as the methyl sulphate salt, clomazone, oxadiazon, bromofenoxim, barban, tridiphane, flurochloridone, quinchlorac and mefanacet;
- BB. Examples of useful contact herbicides include:
  - bipyridylium herbicides such as those in which the active entity is paraquat and those in which the active entity is diquat;
  - \* These compounds are preferably employed in combination with a safener such as dichlormid.

The invention is illustrated by the following Examples. The abbreviations used in the Examples have the following meanings:

NMR spectrum: nuclear magnetic resonance spectrum. (This refers to the proton magnetic resonance spectrum unless otherwise stated). The following abbreviations are used to indicate the multiplicity of the peaks in the NMR spectrum: s (singlet); d (doublet); t (triplet); q (quartet) m (multiplet); br (broad).

IR spectrum: infra-red absorption spectrum.

MS: mass spectrum

GC: gas chromatography      TLC: thin layer chromatography

m.p.: melting point

b.p: boiling point

EXAMPLE 1Preparation of 2,5,7-Trimethyl-1,8-naphthyridin-4-one (Compound No. 1)Step A: 2,6,8-Trimethyl-4H-pyrido[1,2-a]pyrimidin-4-one

A solution of 2-amino-4,6-dimethylpyridine (33.00g) in ethyl acetoacetate (32.30g) was added dropwise to polyphosphoric acid (100ml), with stirring, at 120°C. The mixture was heated to 140-150°C for 3 hours, then cooled, and dissolved in water (300ml). The solution was neutralised with 6M sodium hydroxide solution, and the precipitate was filtered off, washed thoroughly with water and hexane, then dried in vacuo. The title compound was obtained as a pale cream solid, yield 20.00g.

<sup>1</sup>H nmr data (CDCl<sub>3</sub>-d<sub>6</sub>DMSO): δ2.31(6H,s); 3.00(3H,s); 6.07(1H,s); 6.50(1H,broad s); 7.11(1H,broad s).

Step B: 2,5,7-Trimethyl-1,8-naphthyridin-4-one

A solution of 2,6,8-trimethyl-4H-pyrido[1,2-a]-pyrimidin-4-one (Step A above) (20.00g) in diphenyl ether (70ml) was heated under reflux for 4.5 hours, then cooled and diluted with diethyl ether (100ml). The brown precipitate was filtered off, and dissolved in hot methanol (300ml). This solution was treated with decolourising charcoal. The mixture was filtered through hyflo, which was washed with a further 400ml of hot methanol. The combined filtrates were evaporated in vacuo until the volume was about 50ml (a pale yellow crystalline solid began to precipitate out). This was diluted with diethyl ether (80ml), and the product was filtered off and dried. Compound No. 1 was obtained as a pale yellow crystalline solid, yield 12.60g.

EXAMPLE 2

Using essentially the procedure described in Example 1, the compounds listed in Table 3 below were prepared, using the appropriate 2-aminopyridine and beta-keto ester starting materials.



TABLE 3

Compound No	Starting Materials		Appearance of product (and purification method)
	2-Aminopyridine derivative	Beta keto-ester	
2	2-Amino-4,6-dimethyl pyridine	Ethyl propionyl- acetate	white solid
3	"	Ethyl isobutyryl acetate	white solid
4	"	Ethyl benzoyl- acetate	pale cream solid
5	"	Ethyl 2-methyl- acetoacetate	Buff-cream solid (recrystallised from diphenylether/ hexane)
6	"	Ethyl 2-ethyl- acetoacetate	pale buff solid
7	"	Ethyl 2-propyl acetoacetate	pale buff solid (recrystallised from ethyl acetate/hexane)

TABLE 3 continued

Compound No	Starting Materials		Appearance of product (and purification method)
	2-Aminopyridine derivative	Beta keto-ester	
8	"	Ethyl 2-butyl acetoacetate	pale buff solid
9	"	Ethyl 2-isopropyl- acetoacetate	pale buff solid
10	"	Ethyl 2-isobutyl- acetoacetate	yellow solid (purified by SiO <sub>2</sub> gel chromatography in hexane/ethyl acetate)
11	"	Ethyl 2-isopentyl acetoacetate	pale brown solid (recrystallised from ethyl acetate/hexane)
12	"	Ethyl 2-phenyl- acetoacetate	pale cream solid (recrystallised from diphenyl ether/hexane)
13	"	Ethyl 2-benzyl- acetoacetate	pale buff solid (recrystallised from ethyl acetate/hexane)
14	"	Ethyl 2-cyclo- pentanone- carboxylate	brownish solid (recrystallised from methanol/ether)

TABLE 3 continued

Compound No	Starting Materials 2-Aminopyridine derivative	Beta keto-ester	Appearance of product (and purification method)
15	"	Ethyl 2-cyclo- hexanone- carboxylate	pale buff solid (recrystallised from diphenyl ether/ diethyl ether)
16	"	Ethyl trifluoro- acetoacetate	yellow needles (sublimed at 140°C and recrystallised from acetone/methanol) M.Pt 247-248°C
17	2-Amino-6-methyl- pyridine	Ethyl aceto- acetate	pale yellow solid
30	"	Ethyl 2-ethyl acetoacetate	pale brown solid
31	2-Amino-4,6- dimethylpyridine	Methyl 2-oxocyclo- heptane- carboxylate	pale brown solid (recrystallised from methanol/ethyl acetate)
32	"	Methyl 2-methyl- propionyl- acetate	pale brown solid
33	"	Ethyl 2-ethylprop- ionyl-acetate	light brown solid

EXAMPLE 3

Preparation of 2,3,5,6,7-Pentamethyl-1,8-naphthyridin-4-one (Compound No. 34 of Table I)

A solution of 2-amino-4,5,6-trimethylpyridine (5.00g) in ethyl 2-methylacetoacetate (5.29g) was added dropwise to polyphosphoric acid (40ml) at 110°C, with stirring. The mixture was heated at 140°C for 6 hours, then poured onto cracked ice and made slightly basic using 6M sodium hydroxide solution. The precipitate was filtered off, washed with water and acetone, then recrystallised from methanol to give Compound No. 34 as a white, crystalline solid, yield 1.83g.

EXAMPLE 4

Using essentially the procedure described in Example 3, the compounds listed in Table 4 below were prepared, using the appropriate 2-aminopyridine and beta - keto ester starting materials.

TABLE 4

Compound No	Starting Materials		Appearance of product (and purification method)
	2-Aminopyridine derivative	Beta keto-ester	
35	2-Amino-4,5,6-trimethyl)pyridine	Ethyl 2-ethyl-acetoacetate	white solid
36	"	Ethyl 2-n-propyl-acetoacetate	buff solid. (Originally separated as oil, and was extracted with ethyl acetate).
37	"	Ethyl aceto-acetate	white solid (recrystallised from dimethylsulphoxide)

TABLE 4 continued

Compound No	Starting Materials		Appearance of product and purification method
	2-Aminopyridine derivative	Beta keto-ester	
38	2-Amino-5-ethyl- 4,6-dimethyl- pyridine	Ethyl 2-ethyl- aceto- acetate	buff solid (recrystallised from methanol/dimethyl sulphoxide)
39	2-Amino-4,5,6- trimethyl- pyridine	Ethyl 2- ethylpropionyl -acetate	buff solid
40	2-Amino-5,6- dimethylpyridine	Ethyl 2-ethyl acetoacetate	yellow solid (recrystallised from methanol/dimethyl sulphoxide)
50	2-Amino-4,5,6- trimethyl- pyridine	Ethyl 2-iso propyl acetoacetate	pale brown crystals (recrystallised from ethyl acetate/ methanol)
51	2-Amino-6- ethyl-5- methylpyridine	Ethyl 2-ethyl aceto-acetate	cream solid (trituration with hexane)
52	"	Ethyl 2-isoprop- ylacetoacetate	buff solid

TABLE 4 continued

Compound No	Starting Materials 2-Aminopyridine derivative	Beta keto-ester	Appearance of product and purification method
61	"	Ethyl ethyl-propionyl-acetate	cream solid
62	2-Amino-5-ethyl-4,6-dimethylpyridine	Ethyl 2-propyl-acetoacetate	off-white solid
63	"	Ethyl ethyl-propionylacetate	pale yellow solid
64	"	Ethyl 2-isopropyl-acetoacetate	pale brown solid (SiO <sub>2</sub> gel chromatography with ethyl acetate/hexane)

EXAMPLE 5Preparation of 5,7-Dimethyl-1,8-naphthyridin-4-one (Compound No. 18)Step A: Diethyl 2-(4,6-dimethylpyridyl)aminomethylene malonate

A mixture of 2-amino-4,6-dimethylpyridine (12.20g) and diethyl ethoxymethylenemalonate (21.60g) was heated at 110°C until no more ethanol distilled off. On cooling the mixture solidified. This was recrystallised from ethanol to give the title compound as yellow crystals, yield 25.50g. m.pt: 97°C.

Step B: 3-Ethoxycarbonyl-5,7-dimethyl-1,8-naphthyridin-4-one

A solution of diethyl 2-(4,6-dimethylpyridyl)-aminomethylene malonate (step A, above) (25.00g) in diphenyl ether (250ml) was heated, and the ethanol produced was distilled off. Heating was continued until the

distillate temperature reached 240°C. The mixture was then allowed to cool, and was diluted with dichloromethane (100ml). The light brown precipitate was filtered off, washed with dichloromethane, and recrystallised from ethanol to afford the title compound as a pale brown, crystalline solid, yield 10.20g .

m.pt: ca 230°C (decomp).

Step C: 5,7-Dimethyl-1,8-naphthyridin-4-one-3-carboxylic acid

A hot solution of 3-ethoxycarbonyl-5,7-dimethyl-1,8-naphthyridin-4-one (step B, above) (9.90g) in ethanol (350ml) was treated with a solution of potassium hydroxide (2.30g) in ethanol (50ml). The mixture was heated under reflux for 30 minutes, then cooled. The yellow precipitate was filtered off, and washed with ethanol. This was then dissolved in hot 2M hydrochloric acid, and then allowed to cool. The yellow precipitate was filtered off, washed with water, and dried to leave the title compound as a yellow solid, yield 7.00g.

m.pt: > 300°C.

Step D: 5,7-Dimethyl-1,8-naphthyridin-4-one

5,7-Dimethyl-1,8-naphthyridin-4-one-3-carboxylic acid (step C, above) (7.00g) was heated until it melted, and heating was continued until effervescence ceased (some material was lost by sublimation). On cooling the residue solidified. This was recrystallised from xylene to give Compound No. 18 as light brown needles, yield 3.10g.

m.pt: 200°C.

EXAMPLE 6

Preparation of 7-Methyl-1,8-naphthyridin-4-one (Compound No. 19)

By a procedure similar to that described in Example 18, step D but using 7-methyl-1,8-naphthyridin-4-one-3-carboxylic acid (5.00g), Compound No. 19 (3.47g) was obtained as a pale brown solid.

EXAMPLE 7

Preparation of 2-Methyl-1,8-naphthyridin-4-one (Compound No. 20)

Step A: 2-Carbamoylnicotinic acid

A solution of quinolinic anhydride (13.50g) in ethyl methyl ketone (185ml) was treated with dry ammonia gas for 20 minutes. The resultant white precipitate was filtered off, dried, then dissolved in water (100ml) containing 0.880 aqueous ammonia (1ml). This solution was treated with sulphur dioxide gas until precipitation of the product was complete. This was filtered off and dried in vacuo to give Compound No. 20 as a white solid, yield 9.37g.

m.pt: 162°C.

Step B: 3,4-Dihydro-1,3-dioxo-1H-pyrido[2,3-d][1,3]-oxazine

A stirred slurry of 2-carbamoylnicotinic acid (step A, above) (4.00g) in dimethyl formamide (40ml) was treated with lead tetraacetate (11.00g), and the mixture was stirred at 60°C for 1 hour, then poured into water (40ml). The brown precipitate was filtered off and recrystallised from dimethyl formamide-water to give the title compound as a white crystalline solid, yield 2.35g.

m.pt: 218-219°C.

Step C: 3-Ethoxycarbonyl-2-methyl-1,8-naphthyridin-4-one

A 50% dispersion of sodium hydride in oil (2.30g) was washed with hexane (3x20ml), then dimethylformamide (50ml) was added. The resultant slurry was treated dropwise with a solution of ethyl acetoacetate (6.24g) in dimethyl formamide (5ml). After the effervescence ceased, the yellow solution was treated with a hot solution of 3,4-dihydro-1,3-dioxo-1H-pyrido[2,3-d][1,3]oxazine (step B, above) (2.43g) in dimethyl formamide (20ml). The resultant solution was heated to 120°C for 4 hours, then cooled and quenched with water (100ml). The mixture was then neutralised (2M hydrochloric acid) and left to stand for 3 days before being evaporated to dryness (in vacuo). The residue was digested with cold water (20ml) and the product was filtered off, washed with cold water (20ml), hexane, and dried to leave the title compound as a pale buff coloured, microcrystalline solid, yield 1.64g.

<sup>1</sup>H nmr data (CDCl<sub>3</sub>-d<sub>6</sub>DMSO): δ 1.28(3H,t); 2.41(3H,s); 4.24(2H,q); 7.30(1H,dd); 8.43(1H,dd); 8.65(1H,dd).

Step D: 2-Methyl-1,8-naphthyridin-4-one-3-carboxylic acid

A solution of 3-ethoxycarbonyl-2-methyl-1,8-naphthyridin-4-one (step C, above) (0.72g) and potassium hydroxide (1.50g) in ethanol (10ml) and water (10ml) was heated under reflux for 4 hours, then cooled, and acidified to pH5 (2M hydrochloric acid). The white precipitate was filtered off, washed with water and hexane, then dried to leave the title compound as a white solid, yield 0.53g.

<sup>1</sup>H nmr data (CDCl<sub>3</sub>-d<sub>6</sub>DMSO): δ 2.91(3H,s); 7.61(1H,dd); 8.66(1H,dd); 8.92(1H,dd); 13.56(1H,broad s); 15.95(1H,broad s).

Step E: 2-Methyl-1,8-naphthyridin-4-one

By a procedure similar to that describe in Example 5, step D but using 2-methyl-1,8-naphthyridin-4-one-3-carboxylic acid (step D, above ) (0.35g), and recrystallising from methanol-diethyl ether-hexane, Compound No. 20



(0.21g) was obtained as a pale yellow solid.

#### EXAMPLE 8

##### Preparation of 3-Chloro-5,7-dimethyl-1,8-naphthyridin-4-one (Compound No.21)

A solution of potassium chlorate (0.40g) in water (4ml) was added dropwise to a solution of 5,7-dimethyl-1,8-naphthyridin-4-one (Compound No. 18) (0.81g) in concentrated hydrochloric acid (13ml), with ice cooling. The mixture was stirred for a further 10 minutes, then poured carefully into saturated sodium bicarbonate solution. The precipitate was filtered off and recrystallised from ethanol-water to give Compound No. 21 yield 0.30g.

m.pt: 263°C (decomp).

MS: M/Z 208 (M+).

#### EXAMPLE 9

##### Preparation of 3-Chloro-2,5,7-trimethyl-1,8-naphthyridin- 4-one (Compound No. (22))

A solution of potassium chlorate (0.50g) in water (10ml) was added to a stirred suspension of 2,5,7- trimethyl-1,8-naphthyridin-4-one (prepared as in Example 1) (1.90g) in a mixture of concentrated hydrochloric acid (10ml), dimethyl formamide (30ml) and ethanol (10ml). The mixture was stirred for a further 1 hour, then concentrated in vacuo and neutralised with 2M sodium hydroxide solution. The precipitate was filtered off and recrystallised from ethanol to give Compound No. 22 as a pale yellow, crystalline solid, yield 0.70g.

m.pt: >300°C.

MS: M/Z 222(M<sup>+</sup>).

#### EXAMPLE 10

##### Preparation of 3-Chloro-7-methyl-1,8-naphthyridin-4-one (Compound No. 23)

A stirred solution of 7-methyl-1,8-naphthyridin-4-one (Compound No. 19) (0.65g) in acetic acid (10ml) was treated with sulphuryl chloride (0.32ml) at 50°C. The mixture was allowed to cool and stirred for a further 20 minutes, then the white precipitate was filtered off, washed with ether and dried to leave Compound No. 23 as a white powder, yield 0.45g.

#### EXAMPLE 11

##### Preparation of 3-Bromo-5,7-dimethyl-1,8-naphthyridin-4- one (Compound No. 24)

A stirred solution of 5,7-dimethyl-1,8-naphthyridin- 4-one (Compound

No. 18) (0.50g) in acetic acid (4.5ml) was treated with a solution of bromine (0.20ml) in acetic acid (1ml) at 50°C. The orange slurry was stirred for 10 minutes, then the precipitate was filtered off and recrystallised from acetic acid-water to give Compound No. 24 as a buff solid (0.31g).

#### EXAMPLE 12

##### Preparation of 3-Bromo-7-methyl-1,8-naphthyridin-4-one (Compound No. 25)

By a procedure similar to that described in Example 11 but using 7-methyl-1,8-naphthyridin-4-one (Compound No. 19) (1.60g), bromine (0.51ml) and acetic acid (20ml), a crude product was obtained as a buff powder (1.27g). Recrystallisation from acetic acid-water gave a mixture of products (0.72g). Evaporation of the mother liquors (in vacuo) gave Compound No. 25 as a pale brown solid, yield 0.27g.

#### EXAMPLE 13

##### Preparation of 3-Bromo-2,5,7-trimethyl-1,8-naphthyridin-4-one (Compound No. 26)

A solution of 2,5,7-trimethyl-1,8-naphthyridin-4-one (Compound No. 1) (1.40g) in acetic acid (50ml) was treated with bromine (0.38ml). The resulting solution was poured into water, and the precipitate was filtered off and recrystallised from dimethyl formamide to give Compound No. 26 as a pale yellow crystalline solid, yield 1.10g.

MS: M/Z 266 ( $M^+$ ).

#### EXAMPLE 14

##### Preparation of 3-Bromo-5,7-dimethyl-2-trifluoromethyl-1,8-naphthyridin-4-one (Compound No. 27)

By a procedure similar to that described in Example 13 but using 5,7-dimethyl-2-trifluoromethyl-1,8-naphthyridin-4-one (Compound No. 16) (1.10g), bromine (0.3ml) and acetic acid (25ml), and recrystallising from ethanol, Compound No. 27 was obtained as yellow needles (0.73g).

m.pt: 215°C (decomp).

ir. 1635, 1610  $\text{cm}^{-1}$ .

ms m/2 321 ( $M^+$ )

#### EXAMPLE 15

##### Preparation of 3-Iodo-5,7-dimethyl-1,8-naphthyridin-4-one (Compound No. 28)

##### Step A: 3-Carbazoyl-5,7-dimethyl-1,8-naphthyridin-4-one

A solution of 3-ethoxycarbonyl-5,7-dimethyl-1,8-naphthyridin-4-one (prepared as in Example 5 step B) (2.00g) in ethanol (30ml) was treated with hydrazine hydrate (10ml). The mixture was heated under reflux - the

ester slowly dissolved, then a thick white precipitate formed. The mixture was cooled, and the precipitate was filtered off, washed with ethanol, and dried, leaving the title compound as a white solid, yield 1.80g.

mpt: >300°C.

ir: 3340, 3200, 1670, 1655, 1610  $\text{cm}^{-1}$ .

Step B: 3-Iodo-5,7-dimethyl-1,8-naphthyridin-4-one

A suspension of 3-carbazyl-5,7-dimethyl-1,8-naphthyridin-4-one (step A, above) (1.80g) in tetrahydrofuran (50ml) was treated with a solution of sodium hydrogen sulphate (6.50g) in water (40ml). The mixture was heated under reflux, and a solution of iodine (11.50g) in tetrahydrofuran (100ml) was added dropwise. The mixture was stirred for 1 hour, then poured into water (800ml). The mixture was treated with solid sodium thiosulphate until all of the excess iodine was reduced. The mixture was extracted twice with ethyl acetate, and the combined extracts were washed with water, dried ( $\text{MgSO}_4$ ) and evaporated in vacuo to leave an orange solid. This was recrystallised from ethanol to give the Compound No. 28 yield 0.57g.

mpt: 259°C.

ms: m/z 300 ( $\text{M}^+$ ).

EXAMPLE 16

Preparation of 4-Methoxy-2,5,7-trimethyl-1,8-naphthyridine (Compound No. 29.)

2,5,7-Trimethyl-1,8-naphthyridin-4-one (Compound No. 1) (0.95g) was dissolved in a solution of potassium hydroxide (0.27g) in methanol (20ml), and the resulting solution was treated with dimethyl sulphate (0.5ml). The mixture was stirred for 5 hours, then evaporated in vacuo. The residue was digested with water (25ml), and the insoluble solid was filtered off, washed with water, and dried to leave Compound No. 29.

m.pt: 130°C.

MS: M/Z 202 ( $\text{M}^+$ ).

EXAMPLE 17

Preparation of 3-Bromo-2,5,6,7-tetramethyl-1,8-naphthyridin-4-one (Compound No. 41.)

A stirred solution of 2,5,6,7-tetramethyl-1,8-naphthyridin-4-one (Compound No. 37) (0.30g) in acetic acid (7ml) was treated dropwise with bromine (0.235g). A solid formed immediately. Water was added, and the precipitate was filtered off and washed with water to give Compound No. 41 as a yellow solid (0.31g).

EXAMPLE 18Preparation of 6-Bromo-3-ethyl-2,7-dimethyl-1,8-naphthyridin-4-one (Compound No. 30).

A solution of 3-ethyl-2,7-dimethyl-1,8-naphthyridin-4-one (Compound No. 30) (0.34g) in acetic acid, (10ml) was treated with bromine (0.27g), then water (10ml) was added. This mixture was stirred for 30 minutes, then the precipitate was filtered off, and recrystallised from hot (not boiling) dimethyl sulphoxide to give Compound No. 42 as a white, crystalline solid, yield 0.23g.

Using essentially this procedure, the following compounds listed in Table I were prepared.

Compound No. 43 (from Compound 5) (Pale yellow crystals).

Compound No. 44 (from Compound 6) (White crystals).

EXAMPLE 19Preparation of 3,6-Dibromo-5,7-Dimethyl-1,8-naphthyridin-4-one (Compound No. 45).

A solution of 5,7-dimethyl-1,8-naphthyridin-4-one (Compound No. 18) (1.00g) in acetic acid (15ml) was treated dropwise with bromine (0.92g) at 50°C. The yellow-orange precipitate was filtered off and dried (1.00g). Evaporation of the remaining solution gave an orange solid (0.90g). The two solids were combined, and heated in acetic acid (20ml). Water (10ml) was then added. On cooling a white solid precipitated out (0.56g). This was recrystallised from acetic acid to give Compound No. 45 as a white, crystalline solid, yield 0.34g.

(3-Bromo-5,7-dimethyl-1,8-naphthyridin-4-one (Compound No. 24) was obtained from the mother liquors).

EXAMPLE 20Preparation of 2-(Dichloromethyl)-3,5,7-trimethyl-1,8-naphthyridin-4-one (Compound No. 46A), and 2-(Chloromethyl)-3,5,7-trimethyl-1,8-naphthyridin-4-one (Compound No. 46B).

A stirred suspension of 2,3,5,7-tetramethyl-1,8-naphthyridin-4-one (Compound No. 5) (3.00g) in chloroform (100ml) was treated dropwise with sulphuryl chloride (2.20g). The resultant orange solution was stirred for 1 hour, then quenched with saturated sodium bicarbonate solution. The chloroform layer was dried ( $\text{MgSO}_4$ ) and evaporated in vacuo to leave a sticky orange solid. Trituration (ethanol-ether) gave 0.96g of a sandy coloured solid, shown to be unreacted 2,3,5,7-tetramethyl-1,8-naphthyridin-4-one. Evaporation and chromatography of the residue

(Kieselgel 60, eluting with ethyl acetate-hexane mixtures) afforded:  
2-(Dichloromethyl)-3,5,7-trimethyl-1,8-naphthyridin-4-one (Compound No. 46A), 1.00g

m.pt: 184-185°C

and 2-(Chloromethyl)-3,5,7-trimethyl-1,8-naphthyridin-4-one (Compound No. 46B) (0.11g), m.pt 274°C (decomp).

#### EXAMPLE 21

Preparation of 2,3,5,7-Tetramethyl-1,8-naphthyridin-4-one-8-oxide  
(Compound No. 47).

A stirred suspension of 2,3,5,7-tetramethyl-1,8-naphthyridin-4-one (prepared as in Example 5) (15.00g) in dichloromethane (200ml) was treated with a solution of m-chloroperoxybenzoic acid (32.00g) in dichloromethane (200ml). The brown solution was stirred overnight, then quenched with saturated sodium bicarbonate solution. The organic phase was separated and washed with saturated sodium bicarbonate solution (x3) and water, then dried ( $\text{MgSO}_4$ ). Evaporation of the solution in vacuo left a red oil, from which a pale brown solid was obtained by trituration with ether. This was Compound No. 47, yield 2.00g.

m.pt.: sublimes at 240°C.

More of this compound could be obtained from the mother liquors by chromatography. Following essentially the same procedure, but using 3-ethyl-2,5,7-trimethyl-1,8-naphthyridin-4-one (Compound No. 6) as starting material, Compound No. 56 of Table I was obtained as a pale yellow solid.

#### EXAMPLE 22

Preparation of 7-(Acetoxymethyl)-2,3,5-trimethyl-1,8-naphthyridin-4-one (Compound No. 48).

A slurry of crude 2,3,5,7-tetramethyl-1,8-naphthyridin-4-one-8-oxide (Compound No. 47) (15.50g) in acetic anhydride (50ml) was heated to 90°C, then cooled. The resultant black solution was evaporated to dryness in vacuo, and the residue was eluted through a bed of fine silica gel using chloroform, then ethyl acetate. Evaporation of the eluent in vacuo gave a brown solid. This was dissolved in ethyl acetate and washed with saturated sodium bicarbonate solution (x3), dried ( $\text{MgSO}_4$ ), and evaporated in vacuo to leave a brown solid. This was eluted through a silica gel column using chloroform, then ethyl acetate, to give the crude product, which was then triturated with diethyl ether to afford Compound No. 48 as a pale brown powder, yield 2.00g.

m.pt: softens at 166°C, melts at 179°C.

Following essentially the above procedure, but using 3-ethyl-2,5,7-trimethyl-1,8-naphthyridin-4-one-6-oxide (Compound No. 56) as starting material, Compound No. 57 was obtained as a brown solid.

#### EXAMPLE 23

Preparation of 7-(Hydroxymethyl)-2,3,5-trimethyl-1,8-naphthyridin-4-one (Compound No. 49).

A solution of 7-(acetoxymethyl)-2,3,5-trimethyl-1,8-naphthyridin-4-one (Compound No. 48) (1.80g) in methanol (30ml) was treated with Dowex I-X8 resin (OH form) (3.00g). The mixture was stirred for 1 hour, then was filtered through hyflo, washing through with more methanol. Evaporation of the combined filtrates in vacuo left a light brown solid which was triturated with diethyl ether to afford Compound No. 49 as a pale cream powder, yield 1.05g.

Following essentially the above procedure, but using 7 (acetoxymethyl)-3-ethyl-2,5-dimethylnaphthyridin-4-one (Compound No. 57) as starting material, Compound No. 58 was obtained as an off-white powder.

#### EXAMPLE 24

Preparation of 2-(Bromomethyl)-3,7-diethyl-6-methyl-1,8-naphthyridin-4-one (Compound No. 53).

A solution of 3,7-diethyl-2,6-dimethyl-1,8-naphthyridin-4-one (Compound No. 51) (0.20g) in acetic acid (4ml) was treated with bromine (0.137g) followed by water. A trace of solid material which precipitated out was removed by filtration. On standing, a cream precipitate slowly deposited from the filtrate. This was filtered off and dried, affording Compound No. 53 as a cream solid, yield 0.74g.

#### EXAMPLE 25

Preparation of 2,3,5-Trimethyl-1,8-naphthyridin-4-one-7-carboxylic acid (Compound No. 54).

A solution of 7-(hydroxymethyl)-2,3,5-trimethyl-1,8-naphthyridin-4-one (Compound No. 49) (0.40g) in chloroform (10ml) containing methanol (0.5ml) was treated with manganese dioxide (0.90g). The mixture was stirred for 48 hours, then filtered, and the black solid residue was washed with chloroform. This solid was then extracted with saturated aqueous sodium bicarbonate solution (3x10ml). The combined bicarbonate extracts were acidified to pH 1 (conc. hydrochloric acid), and the precipitate was filtered off, washed with water, and dried, to leave Compound No. 54 as a light yellow solid, yield 0.14g.

Following essentially the same procedure, but using 3-ethyl-7-(hydroxy-

methyl)-2,5-dimethyl-1,8-naphthyridin-4-one (Compound No. 58), as starting material, 3-ethyl-2,5-dimethyl-1,8-naphthyridin-4-one-7-carboxylic acid (Compound No. 59) was obtained as a white solid.

#### EXAMPLE 26

Preparation of 2,3,5-trimethyl-1,8-naphthyridin-4-one (Compound No. 55).

2,3,5-Trimethyl-1,8-naphthyridin-4-one-3-carboxylic acid (Compound No. 54) (0.14g) was heated in a test tube (using a gas flame) until the sample blackened and began to sublime. The residue was cooled, and extracted with a hot mixture of chloroform and methanol (9:1). The extract was filtered, and evaporated in vacuo to give Compound No. 55 as a pale brown powder, yield 0.068g.

Following a similar procedure, but using 3-ethyl-2,5-dimethyl-1,8-naphthyridin-4-one-7-carboxylic acid (Compound No. 59) as starting material, 3-ethyl-2,5-dimethyl-1,8-naphthyridin-4-one (Compound No. 60) was obtained as a yellow solid; this was purified by silica gel chromatography using chloroform/methanol as the eluent.

#### EXAMPLE 27

This Example illustrates the herbicidal properties of compounds used in the process of the invention.

The herbicidal activity of the compounds was tested as follows:

Each compound was formulated by dissolving it in an appropriate amount, dependent on the final spray volume, of a solvent/surfactant blend which comprised 78.2 gm/litre of Tween 20 and 21.8 gm/litre of Span 80 adjusted to 1 litre using methylcyclohexanone. Tween 20 is a Trade Mark for a surface-active agent comprising a condensate of 20 molar proportions of ethylene oxide with sorbitan laurate. Span 80 is a Trade Mark for a surface-active agent comprising sorbitan mono-laurate. If the compound did not dissolve, the volume was made up to 5cm<sup>3</sup> with water, glass beads were added and this mixture was then shaken to effect dissolution or suspension of the compound, after which the beads were removed. In all cases, the mixture was then diluted with water to the required spray volume. If sprayed independently, volumes of 25cm<sup>3</sup> and 30cm<sup>3</sup> were required for pre-emergence and post-emergence tests respectively; if sprayed together, 45cm<sup>3</sup> was required. The sprayed aqueous emulsion contained 4% of the initial solvent/surfactant mix and the test compound at an appropriate concentration.

The spray compositions so prepared were sprayed onto young pot plants

(post-emergence test) at a spray volume equivalent to 1000 litres per hectare. Damage to plants was assessed 13 days after spraying by comparison with untreated plants, on a scale of 0 to 9 where 0 is 0% damage, 1 is 1-5% damage, 2 is 6-15% damage, 3 is 16-25% damage, 4 is 26-35% damage, 5 is 36-59% damage, 6 is 60-69% damage, 7 is 70-79% damage, 8 is 80-89% damage and 9 is 90-100% damage.

In a test carried out to detect pre-emergence herbicidal activity, crop seeds were sown at 2 cm depth (i.e. sugar beet, cotton, rape, winter wheat, maize, rice, soya) and weed seeds at 1 cm depth beneath compost and sprayed with the compositions at a spray volume equivalent to 1000 litres per hectare. 20 days after spraying, the seedlings in the sprayed plastic trays were compared with the seedlings in unsprayed control trays, the damage being assessed on the same scale of 0 to 9.

The results of the tests are given in Tables 5 and 6 below. Where no result is given, this is because no test was carried out on the particular species in question.



TABLE 5

Compound			TEST PLANTS															
No	Rate of Appln	Pre- or Post- Emergence Appln	BV	BN	GH	GM	ZM	OS	TA	HV	SU	PA	CA	GA	AR	BP	EH	CO
1	1.0	Post	9	9	3	6	5	3	8		5	9	8	0	5			
	1.0	Pre	0	0	0	0	0	0	0		0	0	0	0	0	0	0	
2	1.0	Post	8	0	0	4	0	0	0		0	8	0	0	3			
	1.0	Pre	2	0	0	0	0	0	0		0	0	0	0	0	0	0	
3	1.0	Post	9	9	0	6	0	0	0		5	9	5	0	0			
	1.0	Pre	0	0	0	0	0	0	0		0	0	0	0	0	0	0	
4	1.0	Post	0	8	2	0	0	0	0		0	5	4	0	0			
	1.0	Pre	0	0	0	0	0	0	0		0	0	0	0	0	0	0	
5	1.0	Post	9	6	7	9	2	2	2		9	9	6	8	3			
	1.0	Pre	0	0	0	0	0	0	0		0	9	0	0	6	0	0	

TABLE 5 (continued)

Compound No	Rate of Appln kg/ha	Pre- or Post- Emergence Appln	TEST PLANTS															
			BV	BN	CH	GM	ZM	OS	TA	HV	SU	PA	CA	GA	AR	BP	EH	CO
6	2.6	Post	9	9	9	9	7	7	9		9	9		9	9	9	8	
	2.6	Pre	9	6	1	0	0	0	7			9		3	5	0		
7	4.0	Pre	6	0	0	0	3	4	0		9	9		9	9	9		
	1.0	Post	8	9	6	9	0	6	8			9	9	7	9	8		
8	1.0	Post	9	9	5	9	5	4	4		9	9		6	9	7		
9	2.6	Post	9	9	5	9	7	7	9		9	9		9	9	7		
	2.6	Pre	9	9	0	0	0	0	4			9		6	5	0		
10	1.0	Post	9	9	5	9	0	5	5			9		2	9	0		

TABLE 5 (continued)

Compound No	Rate of Appln kg/ha	Pre- or Post- Emergence Appln	TEST PLANTS															
			BV	BN	GH	GM	ZM	OS	TA	HV	SU	PA	CA	GA	AR	BP	EH	CO
11	1.0	Post	7	9	3	5	2	3	2			9	9		0	5	4	
12	2.6	Post	7	6	2	2	0	0	0			7	9		2	0	1	
	2.6	Pre	1	0	0	0	0	0	0				9		3	2	0	
13	1.0	Post	9	9	4	6	3	3	2			9	9		0	9	0	
14	1.0	Post	9	2	0	2	0	1	0			3	9		0	0	0	
15	1.0	Post	9	5	7	9	3	1	3			9	9		0	9	8	
	1.0	Pre	0	0	0	0	0	0	0				7		0	0	3	
16	1.0	Post	7	5	5	5	4	4	0			4	0	8	9	7		4
	1.0	Pre	0	4	0	0	0	0	0			5	0		0	4		0

TABLE 5 (continued)

Compound No	Rate of Appln kg/ha	Pre- or Post- Emergence Appln	TEST PLANTS															
			BV	BN	GH	GM	ZM	OS	TA	HV	SU	PA	CA	GA	AR	BP	EH	CO
17	Post	4.0	0	0	3	3	0	0	0	0	0	0	0	0	3	4		
	Pre	4.0	0	0	0	0	0	0	0	0	0	0	0	0	1	0		
19	Post	4.0	3	7	5	4	0	0	0	0	4	8	5	6	4	5		
	Pre	4.0	3	4	5	3	0	3	3	0	0	0	0	0	0	0		
20	Post	4.0	0	0	3	2	0	0	0	0	2	0	0	0	3			
	Pre	4.0	3	3	0	0	0	0	0	0	0	2	4					
21	Post	1.0	7	8	4	0	0	5	4	5	7	4	0	0	5			
	Pre	1.0	8	7	4	0	0	0	0	7	7	0	0	0	0			
22	Post	5.0	8	4	4	7	4	4	4	8	8	8	5	4	8			
	Pre	5.0	9	9	0	4	5	7	8	4	4	0	0	0	7			

TABLE 5 (continued)

Compound			Rate of	Pre- or	TEST PLANTS																
No	Appln		kg/ha	Post-																	
				Emergence	Appln	BV	BN	GH	GM	ZM	OS	TA	HV	SU	PA	CA	GA	AR	BP	EH	CO
23	Post			4.0	0	0	0	0	0	0	0	0		1	5	0	0	0	0	0	
	Pre			4.0	0	0	0	0	0	0	0	0		0	0	0	0	0	0	0	
24	Post			1.0	8	8	7	4	0	0	5	4		7		9	7	8			5
	Pre			1.0	7	8	0	4	0	0	0	0		5	0		0	0			0
25	Post			4.0	4	4	3	3	0	0	0	0			0	4	0	0	0	0	
	Pre			4.0	2	4	0	3	0	0	0	0			0	0	0	0	0	0	
26	Post			1.0	7	4	4	5	4	4	4	4		8	7	8	0	0			8
	Pre			1.0	9	9	4	4	0	5	5	5			0	0	0				4
27	Post			1.0	5	7	4	4	4	4	4	0		7	4	8	8	4			7
	Pre			1.0	5	4		0	5	0	0	0		0	4		5	0			0

TABLE 5 (continued)

Compound No	Rate of Appln kg/ha	Pre- or Post- Emergence Appln	TEST PLANTS															
			BV	BN	GH	GM	ZM	OS	TA	HV	SU	PA	CA	GA	AR	BP	EH	CO
28	Post	1.0	7	7	4	5	5	4	0	5	4	8	8	7			7	
	Pre	1.0	4	5	0	0	0	0	0	0	0		5	0			0	
29	Post	5.0	7	7	4	4	0	4	0	8	5	9	9	7			8	
	Pre	5.0	8	8	4	0	0	4	0		4	7	0	4				
30	Pre	4.0	0	0	0	0	0	2	0			9	0	2	2	0		
	Post	1.0	6	0	2	3	5	1	1		5	9	9	4	9	7		
31	Pre	4.0	4	1	0	0	0	0	0			0	0	0	0	0		
	Post	1.0	9	9	0	0	2	1	0			9	0	0	3	0		
32	Pre	4.0	6	6		0	0				7	9	2	2	2	2		
	Post	1.0	9	9	9	9	3	5	4			9	9	9	9	9		

TABLE 5 (continued)

Compound No	Rate of Appln kg/ha	Pre- or Post- Emergence Appln	TEST PLANTS															
			BV	BN	GH	GM	ZM	OS	TA	HV	SU	PA	CA	GA	AR	BP	EH	CO
33	Pre	4.0	8	9	2	0	0	-	0			9	9	0	0	0	0	0
	Post	1.0	9	9	9	9	6	3	3	-		9	9	9	6	9	9	9
* 34	Post	1.0	5	2	3	3	0	0	4			0	3	0	2	4		
* 35	Post	1.0	9	6	5	5	4	4	5			9	9	4	9	6		
* 36	Post	1.0	9	4	7	3	0	3	0			4	9	6	5	5		
37	Post	1.0	1	0	1	2	1	1	1			0	1	0	0	1		

TABLE 5 (continued)

Compound No	Rate of Appln kg/ha	Pre- or Post- Emergence Appln	TEST PLANTS																
			BV	BN	GH	GM	ZM	OS	TA	HV	SU	PA	CA	GA	AR	BP	EH	CO	
38	Pre	4.0	8	3	0	0	0	0	0	0	5	9	4	2	3				
	Post	1.0	4	3	5	7	5	2	0	9	9	9	9	9	4				
39	Pre	4.0	9	0	0	0	1	9	0	9	6	0	0	0	0				
	Post	0.25	9	3	6	4	0	7	9	9	9	1	0	9	7				
40	Pre	1.0	3	5	5	4	3	2	4	8	6	0	0	3					
	Post	1.0	2	2	3	5	1	1	1	1	1	1	0	1	1				
42	Pre	4.0	4	0	0	0	0	0	0	0	0	0	0	0	0				
	Post	1.0	2	2	0	0	2	0	0	0	0	0	0	2	0				



TABLE 5 (continued)

Compound			Rate of	Pre- or	TEST PLANTS															
No	Appln	kg/ha	Appln	Post-	BV	BN	GH	GM	ZM	OS	TA	HV	SU	PA	CA	GA	AR	BP	EH	CO
43	Pre		4.0		0	0	0	0	0	0	0			5	7	0	0	0	0	
	Post		1.0		3	2	1	2	5	0	1				8	2	4	1	2	
44	Pre		4.0		0	3	0	0	2	0	0			5	7	0	0	0	0	
	Post		1.0		9	8	1	4	5	0	2				9	7	7	7	5	
45	Pre		4.0		0	0	0	0	0	0	0			5	0	0	0	2	0	
	Post		1.0		3	3	0	2	0	0	2				5	0	1	0	0	
46A	Post		4.0		5	6	0	1	1	0	0			2	9	0	2	0	0	
	Pre		4.0		4	0	0	0	0	0	0			0	0	0	0	0	0	
46B	Post		1.0		1	2	0	2	0	0	1			4	9	1	5	1	1	

TABLE 5 (continued)

Compound No	Rate of Appln kg/ha	Pre- or Post- Emergence Appln	TEST PLANTS															
			BV	BN	GH	GM	ZM	OS	TA	HV	SU	PA	CA	GA	AR	BP	EH	CO
47	Post	1.0	9	5	9	7	1	8			9	9	9	9	3	8		
48	Post	1.0	9	2	9	2	1	5			9	9	0	2	2	7		
49	Post	1.0	9	0	9	3	2	3			9	9	9	2	3	7		
50	Post	1.0	9	9	9	4	5	5			9	9	9	9	9	3		
51	Post	1.0	5	0	2	2	1	5			5	8	1	0	0	4		
52	Post	1.0	4	3	3	4	1	0			1	9	3	6	0	3		
53	Post	1.0	1	0	1	3	1	0			1	5	0	0	0	0		

TABLE 5 (continued)

Compound			Rate of	Pre- or	TEST PLANTS																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																	
No	Appln	kg/ha	Post-	Emergence																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																		

\* Applied in a spray volume of 200 litres/hectare

TABLE 6

Compound No	Rate of Appln kg/ha	Pre- or Post- Emergence Appln	TEST PLANTS												
			IH	IL	IX	AT	XP	XT	AF	AM	AE	SH	SV	DS	EC CR CE
1	1.0	Post	4			5		5	9	5	6	8	9	9	5 0
	1.0	Pre		0		0	0		0	0		0	0	0	0
2	1.0	Post	0			0		0	0	3	3	5	5	8	3 0
	1.0	Pre		0		0	0		0	2		0	0	0	0
3	1.0	Post	5			2		0	6	3	5	5	6	5	5 0
	1.0	Pre		0		0	0			0		0	0	0	0
4	1.0	Post	0			0		0	0	5	0	3	0	0	0
	1.0	Pre		0		0	0		0	0		0	0	0	0
5	1.0	Post	7			9		9	9	5	5	5	9	2	0 2
	1.0	Pre		0		0	0		0	0		0	0	2	0

TABLE 6 (continued)

Compound No	Rate of Appln kg/ha	Pre- or Post- Emergence Appln	TEST PLANTS												
			IH	IL	IX	AT	XP	XT	AF	AM	AE	SH	SV	DS	EC CR CE
6	2.6	Post	9		9		9	9	9	7	9	9	9	2	3
	2.6	Pre		7	7	0		3	2		1	5		9	0
7	4.0	Pre			6	0		5	8		5	8		0	0
	1.0	Post	9		9		9	9	9	5	9	9	9	9	0
8	1.0	Post	7		6		9	5	5	6	7	9	9	7	2
9	2.6	Post	2		9		9	9	9	6	9	9	9	7	0
	2.6	Pre		4	9	0		2	5		0	5		5	0
10	1.0	Post	9		9		9	9	6	8	9	9	9	9	2
11	1.0	Post	4		6		5	4	4	4	7	9	9	8	0

TABLE 6 (continued)

Compound No	Rate of Appln kg/ha	Pre- or Post- Emergence Appln	TEST PLANTS												
			IH	IL	IX	AT	XP	XT	AF	AM	AE	SH	SV	DS	EC CR CE
12	2.6	Post	0		3		2	0	0	0	0	0	0	0	0
	2.6	Pre	0		3	0		0	0	0	0	0	0	0	0
13	1.0	Post	4		5		9	5	4	3	9	9	9	6	0
14	1.0	Post	0		2		2	3	2	0	0	0	6	0	0
15	1.0	Post	9		9		9	5	2	3	6	9	9	2	0
	1.0	Pre	0		0	6		1	0	0	0	0	0	0	0
16	1.0	Post		4	7	0		5	4	0	4	7	7	8	0
	1.0	Pre		4	0	0		4	4	0	0	0	0	0	0

TABLE 6 (continued)

Compound No	Rate of Appln kg/ha	Pre- or Post- Emergence Appln	TEST PLANTS												
			IH	IL	IX	AT	XP	XT	AF	AM	AE	SH	SV	DS	EC
			CR	CE											
17	4.0	Post	0		5		3	4	3	0	5	3	0	3	0
	4.0	Pre	0		2	0		0	0		0	4	0	0	0
19	4.0	Post	4		4		0	3	0	0	3	4	5	3	
	4.0	Pre	0		0	0		0	0		0	0	0	0	
20	4.0	Post	2		0		0	0	0	0	0	0	0	0	0
	4.0	Pre	2		2	0		0	0		0	2	0	0	0
21	1.0	Post		8	5	8		4	4	5	4	0	5	7	0
	1.0	Pre		7	0	4		7	4	0	4	0	4	0	0

TABLE 6 (continued)

Compound No	Rate of Appln kg/ha	Pre- or Post- Emergence Appln	TEST PLANTS												
			IH	IL	IX	AT	XP	XT	AF	AM	AE	SH	SV	DS	EC
			CR												
			CE												
22	5.0	Post		5	7	0		7	5	4	5	7	5	4	0
	5.0	Pre		7	8	0		8	8	8	8	8	0	8	8
23	4.0	Post	0		0		0	0	0	0	0	0	0	3	0
	4.0	Pre		0	0	0		0	0	0	0	0	0	0	0
24	1.0	Post		9	8	8		5	5	5	5	9	8	7	0
	1.0	Pre		8	0	0		8	5	0	0	0	0	0	4
25	4.0	Post	3		0		0	3	3	3	5	0	3	0	
	4.0	Pre		0	0	3		0	0	0	0	0	0	0	
26	1.0	Post		5	5	0		7	5	5	5	7	7	4	0
	1.0	Pre		0	9	0		7	8	8	7	4	0	8	0



TABLE 6 (continued)

Compound No	Rate of Appln kg/ha	Pre- or Post-Emergence Appln	TEST PLANTS												
			IH	IL	IX	AT	XP	XT	AF	AM	AE	SH	SV	DS	EC CR CE
27	1.0	Post		7	5	0		4	0	0	0	0	4	5	7 0
	1.0	Pre		0	0	0		0	0	4	0	0	0	0	4 0
28	1.0	Post		7	7	5		4	4	4	5	5	5	7	7 0
	1.0	Pre		0	0	0		4	0	5	0	0	0	0	0 0
29	5.0	Post		7	5	4		4	5	4	4	4	4	4	0 4
	5.0	Pre		0	8	0		7	5	0	0	4	4	0	8 0
30	4.0	Pre		0	0	0		5	0	6	0	6	0	5	0
	1.0	Post	2		6		6	7	1	2	6	9	9	6	0

TABLE 6 (continued)

Compound No	Rate of Appln kg/ha	Pre- or Post- Emergence Appln	TEST PLANTS													
			IH	IL	IX	AT	XP	XT	AF	AM	AE	SH	SV	DS	EC	CR CE
31	4.0	Pre			0		0	0	0	0	0	0	0	0	0	0
	1.0	Post	1		3		0	5	1	2	7	9	9	9	6	0
32	4.0	Pre		3	5		3	0	0		2	5	-	3	3	
	1.0	Post	9		9		9	5	5	4	9	9	9	9	5	2
33	4.0	Pre		0	4		2	2	0		0	8	-	4	0	
	1.0	Post	9		9		9	5	5	4	9	9	9	9	6	4
34	1.0	Post	0		0		0	0	0	0	4	0	5			0
35	1.0	Post	6		5		9	3	5	9	9	4				0

TABLE 6 (continued)

Compound No	Rate of Appln kg/ha	Pre- or Post- Emergence Appln	TEST PLANTS														
			IH	IL	IX	AT	XP	XT	AF	AM	AE	SH	SV	DS	EC	CR	CE
36	1.0	Post	3		5		9		5	0	6	5	5			0	
37	1.0	Post	0		1		1	1	0	1	1	0	8	2		0	
38	4.0	Pre		0	6		5	0	0		0	5		5		0	
	1.0	Post	5		5		9	4	5	5	7	9	9	8		3	
39	4.0	Pre		0	0		0	0	0		0	0	0	5		0	
	0.25	Post	9		9		5	3	0	7	5	9	6	2		0	
40	1.0	Post	0		4		5	9	3	5	5	9	9	6		0	

TABLE 6 (continued)

Compound No	Rate of Appln kg/ha	Pre- or Post- Emergence Appln	TEST PLANTS												
			IH	IL	IX	AT	XP	XT	AF	AM	AE	SH	SV	DS	EC CR CE
41	1.0	Post	0		0		3	4	1	3	4	6	9	5	0
42	4.0	Pre	0		1		6	0	0		0	1		6	0
	1.0	Post	0		0		0	2	0	0	2	0	4	0	0
43	4.0	Pre	3		0		0	0	0		0	0		0	0
	1.0	Post	4		1		4	2	0	3	3	3	8	4	0
44	4.0	Pre	0		3		0	0	0		0	0		0	0
	1.0	Post	3		3		7	3	3	5	5	7	8	5	0

TABLE 6 (continued)

Compound No	Rate of Appln kg/ha	Pre- or Post- Emergence Appln	TEST PLANTS												
			IH	IL	IX	AT	XP	XT	AF	AM	AE	SH	SV	DS	EC CR CE
45	4.0	Pre		0		0	0	0	0	0	0	0	0	-	0 0
	1.0	Post	0		1	1	2	2	3	0	0	0	0	5	4 0
46A	4.0	Post	0		3	0	1	1	0	3	7	6	2	0	0
	4.0	Pre	0		0	3	0	0	6	0	-	0	0	0	0
46B	1.0	Post	0		0	0	2	1	3	7	9	7	7	3	
47	1.0	Post	9		9		5	1	6	2	8	9	4	1	
48	1.0	Post	9		5		5	2	7	2	4	9	5	0	
49	1.0	Post	9		2		7	2	6	2	2	5	2	0	

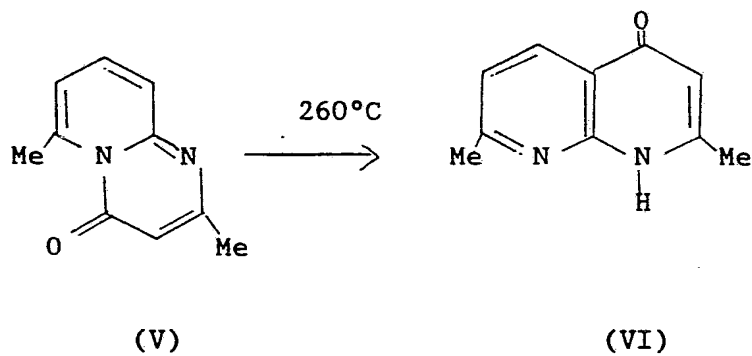
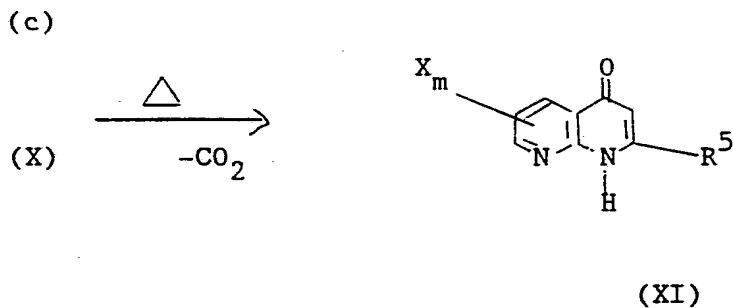
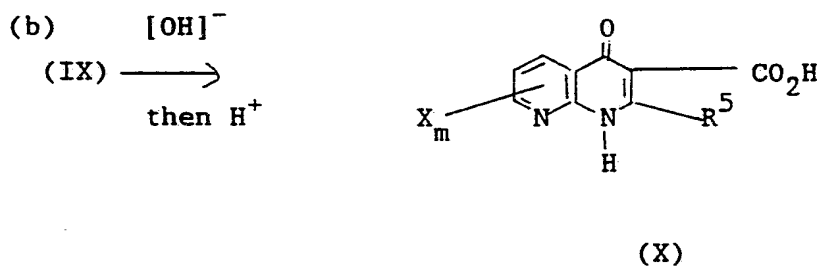
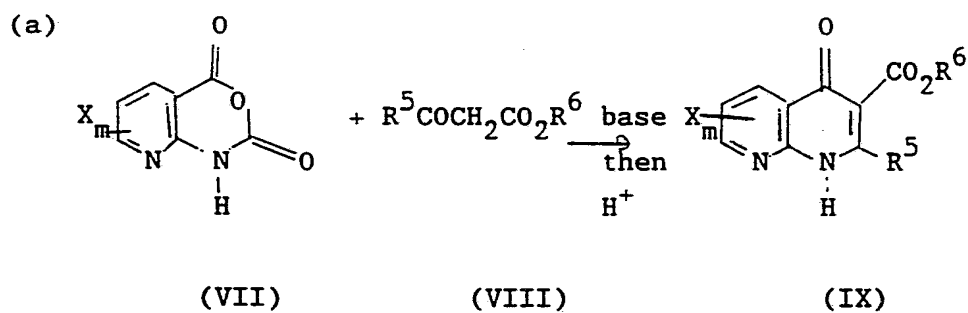
TABLE 6 (continued)

Compound No	Rate of Appln kg/ha	Pre- or Post- Emergence Appln	TEST PLANTS															
			IH	IL	IX	AT	XP	XT	AF	AM	AE	SH	SV	DS	EC	CR	CE	
50	1.0	Post	0		7		9	5	4	6	3	8	9	4		0		
51	1.0	Post	1		1		1	9	2	5	3	4	9	0				
52	1.0	Post	2		2		5	4	2	1	2	9	9	5				
53	1.0	Post	0		0		2	0	1	4	1	0	1	1	1			
55	1.0	Post	5		9		9	6	6	9	4	8	7	9		-		
56	1.0	Post	9		6		9	9	7	5	8	8	3	9		-		
58	1.0	Post	9		9		9	9	9	7	8	9	7	4	1			
60	1.0	Post	9		7		9	9	9	5	7	9	9	6	5			
61	1.0	Post	2		5			3	2		5	7	6	3		2		

\* Applied in a spray volume of 200 litres/hectare

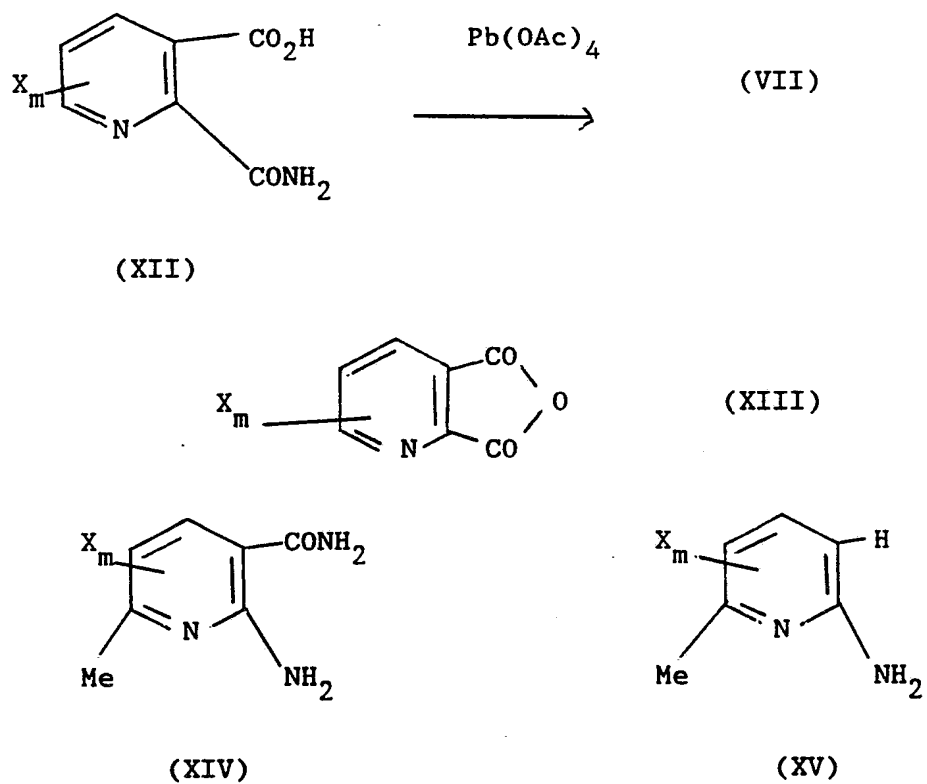
TABLE 7Abbreviations used for Test Plants

BV	-	Sugar beet
BN	-	Rape
GH	-	Cotton
GM	-	Soybean
ZM	-	Maize
OS	-	Rice
TA	-	Winter wheat
HV	-	<u>Hordeum vulgare</u>
SU	-	<u>Senecio vulgaris</u>
PA	-	<u>Polygonum aviculare</u>
CA	-	<u>Chenopodium album</u>
GA	-	<u>Galium aparine</u>
AR	-	<u>Amaranthus retroflexus</u>
BP	-	<u>Bidens pilosa</u>
EH	-	<u>Euphorbia heterophylla</u>
CO	-	<u>Cassia obtusifolia</u>
IH	-	<u>Ipomoea hederacea (post-emergence)</u>
IL	-	<u>Ipomoea lacunosa (pre-emergence)</u>
IX	-	<u>Ipomoea ssp</u>
AT	-	<u>Abutilon theophrasti</u>
XP	-	<u>Xanthium spinosum</u>
XT	-	<u>Xanthium strumarium</u>
AF	-	<u>Avena fatua</u>
AM	-	<u>Alopecurus myosuroides</u>
AE	-	<u>Elymus repens</u>
SH	-	<u>Sorghum halepense</u>
SV	-	<u>Setaria viridis</u>
DS	-	<u>Digitaria sanguinalis</u>
EC	-	<u>Echinochloa crus-galli</u>
CR	-	<u>Cyperus rotundus</u>
CE	-	<u>Cyperus esculentus</u>

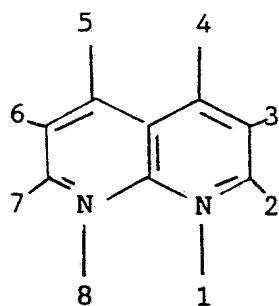
Scheme AScheme B



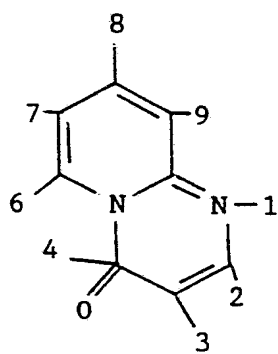
Scheme C



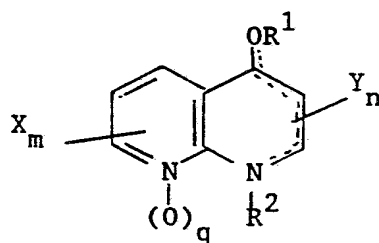
CHEMICAL FORMULAE  
(in description)



(II)



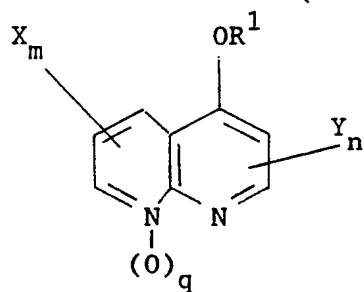
(III)



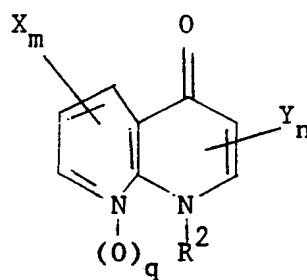
(I)

## CHEMICAL FORMULAE (continued)

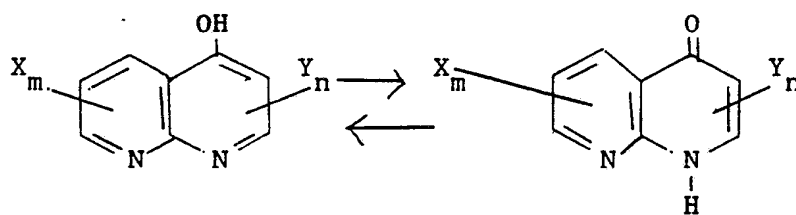
(in description)



(Ia)

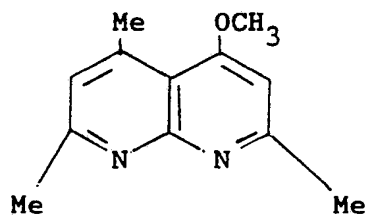


(Ib)

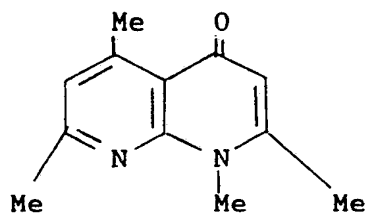


IVa

IVb

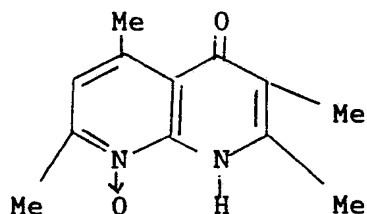


(XVI)

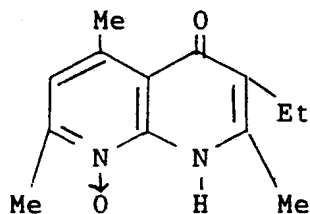


(XVII )

(XVIA)

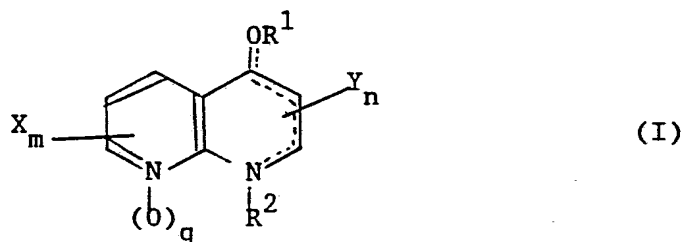


(XVIII)



CLAIMS

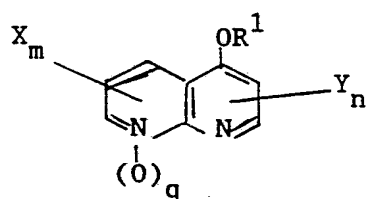
1. A process of severely damaging or killing unwanted plants, which comprises applying to the plants, or to the growth medium of the plants, a herbicidally effective amount of a naphthyridine compound of the formula (I):



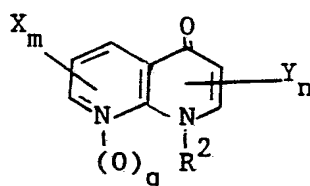
wherein either (a)  $R^1$  is a hydrogen atom, a lower acyl group, or an optionally substituted lower hydrocarbyl group, in which case no group  $R^2$  is present,

or (b)  $R^2$  is a hydrogen atom, an optionally substituted lower hydrocarbyl group or a lower acyl group, in which case no group  $R^1$  is present;

the dashed line between the oxygen atom and the nitrogen atom of the right-hand ring represents two double bonds which may be arranged either as in formula (Ia) or (Ib):



(Ia)



(Ib)

and each of X and Y, which may be the same or different, may stand for fluorine, chlorine, bromine, or iodine; an optionally substituted lower hydrocarbyl group; an optionally substituted lower hydrocarbyl-thio, -sulphinyl, or -sulphonyl group; a carboxyl group or a salt, amide, or ester thereof; a cyano group; a nitro group; an  $-NR^3R^4$  group wherein  $R^3$  and  $R^4$  may each stand independently for hydrogen, optionally substituted lower hydrocarbyl, lower alkylcarbonyl, lower alkoxy carbonyl or lower alkoxy, or  $R^3$  and  $R^4$ ,

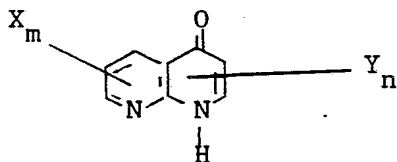
together with the nitrogen atom to which they are attached, form a pyrrolidino, piperidino, or morpholino ring optionally substituted by one or more methyl groups; or each of X and Y may independently stand for an optionally substituted tri-, tetra- or penta-methylene group or a propenylene or butadienylene group wherein in the case of X the terminal valencies are attached to either the 5,6- or the 6, 7-positions or in the case of Y to the 2,3- positions of the naphthyridine nucleus;

m is 0, 1, 2, or 3;

n is 0, 1 or 2.

and q is 0 or 1.

2. A process as claimed in claim 1, wherein the group  $R^1$  in the compound of formula I is hydrogen.
3. A process as claimed in claim 2, wherein the groups X and Y in the compound of formula I comprise at least three methyl or ethyl groups.
4. A process as claimed in claim 2 or claim 3, wherein the group  $X_m$  comprises a  $C_{1-3}$  alkyl group in the 7- position of the naphthyridine ring, and a methyl or ethyl group in one or both of the 5- and 6- positions of the naphthyridine ring; and the group  $Y_n$  comprises a methyl or ethyl group at the 2- position and a  $C_{1-3}$  alkyl group or a bromine or iodine atom at the 3- position; or the group  $Y_n$  comprises a 1,4-tetramethylene or 1,5-pentamethylene group linked to the 2- and the 3- positions to form a 6- or 7- membered ring.
5. Herbicidal compositions comprising as an active ingredient a compound of the formula (I) as defined in any of claims 1 to 4 in association with a carrier comprising a solid or liquid diluent.
6. Herbicidal compositions as claimed in claim 5 which further comprise a surface-active agent.
7. Naphthyridine compounds of formula:



wherein the group  $X_m$  comprises a  $C_{1-3}$  alkyl substituent in the 7-position of the naphthyridine ring, and a methyl or ethyl group in one or both of the 5- and 6- positions; and the group  $Y_n$  comprises a methyl or ethyl substituent at the 2- position of the naphthyridine ring; a  $C_{1-3}$  alkyl substituent or a bromo or iodo substituent at the 3- position; or the group  $Y_n$  comprises a 1,4- tetramethylene or 1,5-pentamethylene group linked to the 2- and the 3- position to form, together with the carbon atoms to which they are attached, a 6- or 7-membered ring, provided that the compounds 2,3,5,7- tetramethyl-1,8-naphthyridin-4-one and 3-ethyl-2,5,7-trimethyl-1,8-naphthyridin-4-one are excluded.

8. A compound as claimed in claim 7 wherein the 3- position of the naphthyridine ring bears a  $C_{1-3}$  alkyl substituent.
9. A naphthyridine compound is claimed in claim 7 or claim 8 which is 3-isopropyl-2,5,7-trimethyl-1,8-naphthyridin-4-one, 3,6-diethyl-2,5,7-trimethyl-1,8-naphthyridin-4-one, 5,7-dimethyl-2,3-tetramethylene-1,8-naphthyridin-4-one, or 5,7-dimethyl-2,3-pentamethylene-1,8-naphthyridine-4-one.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 91/01759

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC <b>IPC5: A 01 N 43/90, C 07 D 471/04/(C 07 D 471/04, 221:00)</b>														
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched<sup>7</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border: 1px solid black; text-align: left;">Classification System</th> <th style="border: 1px solid black; text-align: left;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; height: 40px; vertical-align: bottom;">IPC5</td> <td style="border: 1px solid black; vertical-align: bottom;">A 01 N; C 07 D</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched<sup>8</sup></div>			Classification System	Classification Symbols	IPC5	A 01 N; C 07 D								
Classification System	Classification Symbols													
IPC5	A 01 N; C 07 D													
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; border: 1px solid black;">Category *</th> <th style="width: 70%; border: 1px solid black;">Citation of Document,<sup>11</sup> with indication, where appropriate, of the relevant passages<sup>12</sup></th> <th style="width: 20%; border: 1px solid black;">Relevant to Claim No.<sup>13</sup></th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;">CH, A5, 617693 (CHINOIN GYOGYSZER- ES VEGYESZETI TERMEKEK GYARA RT) 13 June 1980, see the claims; page 2 lines 19-22  --</td> <td style="text-align: center; vertical-align: top;">1-6</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;">CH, A5, 617198 (CHINOIN GYOGYSZER- ES VEGYESZETI TERMEKEK GYARA RT) 14 May 1980, see the claims; page 2 lines 28-31  ---</td> <td style="text-align: center; vertical-align: top;">1-6</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;">Patent Abstracts of Japan, Vol 13, No 331, C622, abstract of JP 01-110603, publ 1989-04-27 SDS BIOTECH K.K. et al.  ---</td> <td style="text-align: center; vertical-align: top;">1-6</td> </tr> </tbody> </table>			Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	X	CH, A5, 617693 (CHINOIN GYOGYSZER- ES VEGYESZETI TERMEKEK GYARA RT) 13 June 1980, see the claims; page 2 lines 19-22  --	1-6	X	CH, A5, 617198 (CHINOIN GYOGYSZER- ES VEGYESZETI TERMEKEK GYARA RT) 14 May 1980, see the claims; page 2 lines 28-31  ---	1-6	X	Patent Abstracts of Japan, Vol 13, No 331, C622, abstract of JP 01-110603, publ 1989-04-27 SDS BIOTECH K.K. et al.  ---	1-6
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X	CH, A5, 617693 (CHINOIN GYOGYSZER- ES VEGYESZETI TERMEKEK GYARA RT) 13 June 1980, see the claims; page 2 lines 19-22  --	1-6												
X	CH, A5, 617198 (CHINOIN GYOGYSZER- ES VEGYESZETI TERMEKEK GYARA RT) 14 May 1980, see the claims; page 2 lines 28-31  ---	1-6												
X	Patent Abstracts of Japan, Vol 13, No 331, C622, abstract of JP 01-110603, publ 1989-04-27 SDS BIOTECH K.K. et al.  ---	1-6												
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><b>* Special categories of cited documents:<sup>10</sup></b></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>														
<b>IV. CERTIFICATION</b> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border: 1px solid black; padding: 5px;">           Date of the Actual Completion of the International Search   <b>18th December 1991</b> </td> <td style="width: 50%; border: 1px solid black; padding: 5px;">           Date of Mailing of this International Search Report   <b>14. 01. 92</b> </td> </tr> <tr> <td style="border: 1px solid black; padding: 5px;">           International Searching Authority   <b>EUROPEAN PATENT OFFICE</b> </td> <td style="border: 1px solid black; padding: 5px;">           Signature of Authorized Officer   <div style="text-align: right;"> <b>Nicole De Bie</b> </div> </td> </tr> </table>			Date of the Actual Completion of the International Search  <b>18th December 1991</b>	Date of Mailing of this International Search Report  <b>14. 01. 92</b>	International Searching Authority  <b>EUROPEAN PATENT OFFICE</b>	Signature of Authorized Officer  <div style="text-align: right;"> <b>Nicole De Bie</b> </div>								
Date of the Actual Completion of the International Search  <b>18th December 1991</b>	Date of Mailing of this International Search Report  <b>14. 01. 92</b>													
International Searching Authority  <b>EUROPEAN PATENT OFFICE</b>	Signature of Authorized Officer  <div style="text-align: right;"> <b>Nicole De Bie</b> </div>													

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
X	II Farmaco - Ed.Sc., vol. 28, No. 9, 1973, S. Carboni et al.: "Sintesi ed attivita biologica di alcune 1,8-naftiridine ", see page 722 - page 732	5-9
A	--	1-4
X	Journal of heterocyclic chemistry, vol. 16, April 1979, F. Fülöp et al.: "Nitrogen Bridgehead Compounds. IX. Synthesis and Reactions of 2,3-Disubstituted Pyrido(1,2-a)pyrimidin-4-ones (1) ", see page 457 - page 460 see page 459 Table II	7-9
A	--	1-4
X	Journal of heterocyclic chemistry, vol. 20, 1983, Pier Luigi Ferrarini et al.: "Synthesis of some Substituted Pyrido(1,2-a)pyrimidin-4-ones and 1,8-Naphthyridines ", see page 1053 - page 1057 see page 1055, Table II	7-9
A	--	1-6
X	Chemical society. London Journal. Perkin transactions, 1977, Istvan Hermecz et al.: "Nitrogen Bridgehead Compounds. Part 4.1 1 - 3N - C-acyl Migration. Part 2 1 ", see page 789 - page 795 see page 791, Table 2	7-9
A	--	1-6
A	DE, A1, 3907937 (BASF AG) 13 September 1990, see the claims; page 14 line 1 - page 15 line 24	1-6
A	--	1-6
A	EP, A2, 0329012 (BASF AKTIENGESELLSCHAFT) 23 August 1989, see the claims	1-6
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	<p>Chemical Abstracts, volume 82, no. 7, 17 February 1975, (Columbus, Ohio, US), Hamada Yoshiki et al.: "Nitrogen-containing heterocyclic compounds. XXI. Syntheses of naphthyridines by improved one step process.", see page 422, abstract 43211e, &amp; Yakugaku Zasshi 1974, 94(10), 1328-1334</p> <p style="text-align: center;">-- -----</p>	1-6

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO. PCT/GB 91/01759**

SA 51895

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 31/10/91. The European Patent office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CH-A5- 617693	13/06/80	AT-B- 337196	10/06/77
		AT-B- 338815	12/09/77
		CA-A- 1039285	26/09/78
		CA-A- 1044238	12/12/78
		CA-A- 1051434	27/03/79
		CA-A- 1053234	24/04/79
		CH-A- 612967	31/08/79
		CH-A- 613968	31/10/79
		CH-A- 617198	14/05/80
		DE-A- 2433840	06/02/75
		FR-A-B- 2237899	14/02/75
		GB-A- 1481601	03/08/77
		GB-A- 1493947	30/11/77
		GB-A- 1493948	30/11/77
		GB-A- 1493949	30/11/77
		GB-A- 1493950	30/11/77
		JP-A- 50100092	08/08/75
		JP-A- 50157395	19/12/75
		JP-A- 51004197	14/01/76
		JP-A- 51023297	24/02/76
		NL-A- 7416923	01/07/75
		NL-A- 7416925	01/07/75
		NL-A- 7416926	01/07/75
		NL-A- 7416927	01/07/75
		NL-A- 7900400	31/05/79
		SE-B-C- 419862	31/08/81
		SE-B-C- 419863	31/08/81
		SE-A- 7416320	30/06/75
		SE-A- 7416321	30/06/75
		SE-A- 7416322	30/06/75
		SE-A- 7416323	30/06/75
		AT-B- 340943	10/01/78
CH-A5- 617198	14/05/80	AT-B- 337196	10/06/77
		AT-B- 338815	12/09/77
		CA-A- 1039285	26/09/78
		CA-A- 1044238	12/12/78
		CA-A- 1051434	27/03/79
		CA-A- 1053234	24/04/79
		CH-A- 612967	31/08/79
		CH-A- 613968	31/10/79
		CH-A- 617693	13/06/80
		DE-A- 2433840	06/02/75
		FR-A-B- 2237899	14/02/75

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**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO. PCT/GB 91/01759**

SA 51895

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 31/10/91. The European Patent office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
CH-A5- 617198	14/05/80	GB-A-	1481601	03/08/77
		GB-A-	1493947	30/11/77
		GB-A-	1493948	30/11/77
		GB-A-	1493949	30/11/77
		GB-A-	1493950	30/11/77
		JP-A-	50100092	08/08/75
		JP-A-	50157395	19/12/75
		JP-A-	51004197	14/01/76
		JP-A-	51023297	24/02/76
		NL-A-	7416923	01/07/75
		NL-A-	7416925	01/07/75
		NL-A-	7416926	01/07/75
		NL-A-	7416927	01/07/75
		NL-A-	7900400	31/05/79
		SE-B-C-	419862	31/08/81
		SE-B-C-	419863	31/08/81
		SE-A-	7416320	30/06/75
		SE-A-	7416321	30/06/75
		SE-A-	7416322	30/06/75
		SE-A-	7416323	30/06/75
		AT-B-	340943	10/01/78
DE-A1- 3907937	13/09/90	CA-A-	2011538	11/09/90
		EP-A-	0387568	19/09/90
		JP-A-	2268183	01/11/90
EP-A2- 0329012	23/08/89	DE-A-	3804990	31/08/89
		JP-A-	1254682	11/10/89
		US-A-	4881969	21/11/89
		US-A-	4999044	12/03/91
		US-A-	4999045	12/03/91

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